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Counterion Effects in Decatungstate Photocatalysis

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ABSTRACT

Photocatalysis with decatungstate ($[\text{W}_{10}\text{O}_{32}]^{4-}$, DT) is a versatile platform for hydrogen-atom-transfer (HAT)-mediated C–H functionalization under mild conditions. Decatungstate is valued for its ability to abstract hydrogen from strong aliphatic, benzylic, allylic, and α -heteroatom C–H bonds. Its efficiency is often attributed to the excited-state reactivity of $[\text{W}_{10}\text{O}_{32}]^{4-}$ and substrate C–H bond strength, but this view neglects the vital role of counterions, which are integral to the catalytic system and influence performance. In solution, DT forms dynamic ion-paired ensembles where counterions affect solubility, substrate access, ion pairing, aggregation, and photostability. These factors impact activity, selectivity, productivity, and robustness. This perspective discusses counterion effects across various systems, including sodium, tetrabutylammonium, phosphonium derivatives, ionic liquids, and immobilized platforms. It highlights counterions as active components that govern catalytic parameters, aiding better catalyst design and system development.

1 | Introduction—Beyond the “Spectator” Counterion

Decatungstate photocatalysis has emerged as one of the most powerful and versatile platforms for hydrogen-atom-transfer (HAT)-mediated C–H functionalization reactions [1–4]. Upon photoexcitation, the decatungstate anion ($[\text{W}_{10}\text{O}_{32}]^{4-}$) can abstract hydrogen atoms from C–H bonds with bond dissociation energies of up to $\sim 105 \text{ kcal mol}^{-1}$ [5], enabling selective functionalization of benzylic, allylic, α -heteroatom (O, N, S, and Si), and even unactivated aliphatic C–H bonds under mild reaction conditions [3, 4, 6, 7]. Its predictable site selectivity, arising from the interplay of bond dissociation energies, polarity effects, electronic factors, and steric accessibility, together with its broad functional-group tolerance, has established decatungstate as one of the most widely used HAT photocatalysts in modern synthetic chemistry [1–6].

Despite this remarkable synthetic success, mechanistic discussions of decatungstate photocatalysis have remained largely

centered on an anion-centric framework [6, 8–10]. Reactivity is typically rationalized in terms of the excited-state electronic structure of the $[\text{W}_{10}\text{O}_{32}]^{4-}$ cluster and the thermodynamics of hydrogen-atom transfer, with substrate-dependent factors such as C–H bond strength, steric effects, and polarity governing site selectivity. Within this framework, counterions are generally regarded as passive species that serve primarily to maintain the charge balance. Consequently, catalyst optimization is often performed with the anionic component held constant, while the variation of the counteranion is treated as a secondary, empirically screened parameter. However, increasing experimental evidence demonstrates that counterion identity can profoundly influence reaction kinetics, product yield, selectivity, catalyst stability, and overall catalytic efficiency.

In photoredox and energy-transfer catalysis, the mechanistic importance of ion pairing has become increasingly evident. Counterions have been shown to influence excited-state lifetimes, charge-separation dynamics, energy-transfer efficiencies, aggregation

In memory of Prof. Dr. Henning Hopf.

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behavior, and overall catalytic performance [11–15]. These findings establish ion pairing as a mechanistically relevant parameter rather than merely a structural feature. A similar paradigm is now emerging in decatungstate photocatalysis. Consistent with the growing recognition of ion-pairing effects in photoredox and energy-transfer catalysis, the decatungstate functions as an ionic assembly in which the $[\text{W}_{10}\text{O}_{32}]^{4-}$ anion and its counterions remain associated to varying degrees, depending on the solvent and reaction conditions. Consequently, counterions influence catalyst solubility and may affect ion-pairing equilibria, aggregation behavior, photostability, substrate accessibility, and interfacial organization. Decatungstate photocatalysts are therefore more appropriately viewed as dynamic ion-paired systems rather than isolated anionic species, particularly under conditions where counterion-dependent effects become significant.

The frequently observed differences between sodium decatungstate (NaDT) and tetrabutylammonium decatungstate (TBADT), the two most widely used decatungstate photocatalysts, demonstrate that catalytic performance is governed not only by the intrinsic photochemical properties of the $[\text{W}_{10}\text{O}_{32}]^{4-}$ core but also by the nature of the associated counterion and the resulting supramolecular organization of the catalytic system. In addition, the choice of the counterion can influence the practical stability and applicability of the decatungstate in different reaction media. In particular, the use of decatungstate photocatalysts in aqueous media is constrained by the pH- and time-dependent stability of $[\text{W}_{10}\text{O}_{32}]^{4-}$. In aqueous media, the decatungstate anion has been detected over a pH range of 2.0–5.0, but undergoes time-dependent speciation into other isopolyoxotungstate species, thereby reducing the concentration of decatungstate available for photocatalysis [16, 17]. Consequently, acidic aqueous media are generally required to minimize decatungstate anion speciation during catalysis [16–18]. This consideration is particularly relevant when sodium decatungstate is employed in aqueous organic solvent mixtures. Conversely, catalyst stability may also be compromised by degradation of the counterion itself under photocatalytic conditions, as demonstrated for tetraalkylammonium decatungstate salts [19, 20].

Counterions therefore emerge as key determinants of reaction efficiency, selectivity, and operational robustness, placing them alongside the polyoxometalate anion as fundamental components of decatungstate catalysis (Scheme 1) [21, 22]. Beyond these benchmark systems, decatungstate chemistry encompasses a structurally diverse family of catalysts, including alkali metal, tetraalkylammonium, tetraalkylphosphonium, tetraphenylphosphonium, ionic-liquid-based, surfactant-derived, and immobilized systems [21–28].

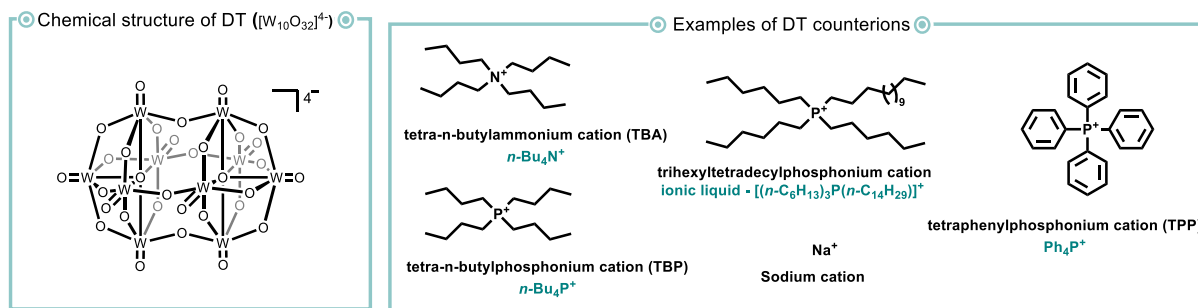
Collectively, these platforms define a largely underexplored design space in which counterion selection can tune the catalytic behavior in ways that extend far beyond simple solubility control.

Numerous reviews have comprehensively addressed the synthetic scope, mechanistic aspects, and recent advances in decatungstate photocatalysis, as well as its broader applications in hydrogen-atom-transfer chemistry [2–4]. Most recently, a comprehensive perspective has examined decatungstate photocatalysis from a process-oriented viewpoint, critically evaluating reaction development, catalyst performance, scalability, and the challenges associated with translating this photocatalytic platform from laboratory methodology to industrial application [29]. Taking a different angle, the present perspective focuses on an aspect that has received comparatively little attention despite growing evidence for its mechanistic importance: the role of counterions. To address this dimension, we systematically examine how counterion identity influences decatungstate photocatalysis across homogeneous, heterogeneous, and hybrid reaction environments. By correlating the ion-pair structure with photochemical behavior and catalytic outcomes, we highlight counterions as integral components of the catalytic ensemble rather than passive spectators. Furthermore, we discuss how counterion engineering can serve as a strategic tool for the rational design of next-generation decatungstate photocatalysts and related photochemical systems.

2 | Historical Development of Decatungstate Photocatalysis in Synthetic Transformations

Polyoxometalates (POMs) constitute a well-established class of discrete metal–oxide clusters with broad relevance in catalysis, materials science, and redox chemistry. Their structural and chemical features have been extensively elucidated through decades of experimental investigation [30–37]. Foundational work by Pope and coworkers in the 1980s provided a comprehensive framework for understanding their structural, electronic, and redox properties, establishing POMs as robust, molecularly defined inorganic architectures with high structural integrity and tunable redox behavior [38]. Within this broader family, the decatungstate anion ($[\text{W}_{10}\text{O}_{32}]^{4-}$, DT) has emerged as one of the most effective photocatalytic platforms.

Pioneering studies by Hill and coworkers and Tanielian in the 1990s were instrumental in establishing the photochemical behavior of polyoxometalates, demonstrating that photoexcited



SCHEME 1 | Chemical structures of the decatungstate anion and representative counterions discussed in this perspective.

POMs can engage in both electron-transfer and hydrogen-atom-transfer processes depending on the reaction environment [10, 39]. Within this context, decatungstate was identified as a particularly powerful HAT photocatalyst capable of activating strong, otherwise inert C–H bonds under UV irradiation via ligand-to-metal charge-transfer (LMCT) excitation. These mechanistic insights enabled the first synthetic applications of the decatungstate, initially focused on simple hydrocarbon substrates and demonstrating the feasibility of selective C–H bond activation under mild conditions. Over time, these early studies evolved beyond simple hydrocarbon functionalization to encompass increasingly complex molecular scaffolds [40–43].

A key milestone in this development was the transition of decatungstate photocatalysis from fundamental mechanistic investigation to a broadly applicable synthetic methodology [44–46]. This expansion was accompanied by a rapid diversification of reaction manifolds, including Giese-type additions, C–H alkylations, oxidations, halogenations, radical cascade cyclizations, and late-stage functionalization of complex molecules [5, 47–55]. In many cases, decatungstate-mediated transformations enable reactivity that remains challenging under conventional thermal catalysis, particularly because they can directly activate strong, unactivated C–H bonds without prefunctionalization. As these applications expanded, decatungstate photocatalysis became established as a general platform for hydrogen-atom-transfer-mediated C–H functionalization, valued for its broad substrate scope, predictable reactivity, and operational simplicity. It is now recognized as one of the most widely utilized systems in HAT chemistry and continues to underpin modern strategies for C–H bond activation.

3 | Photophysics and Excited-State Reactivity of Decatungstate

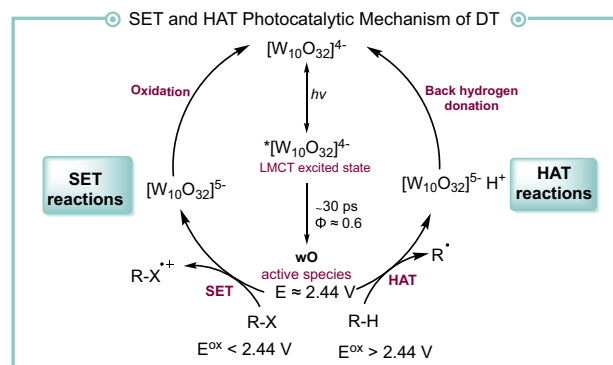
Upon irradiation with UV or near-UV light (typically 320–400 nm), the decatungstate anion ($[W_{10}O_{32}]^{4-}$) undergoes oxygen-to-tungsten ligand-to-metal charge-transfer (LMCT) excitation, involving promotion of electrons from O 2p orbitals into W 5d-based acceptor states [9]. These LMCT transition gives rise to intense absorption bands in the near UV region, with a maximum at 324 nm and a tail extending towards longer wavelengths, thereby enabling photocatalysis under relatively mild irradiation conditions. Following photoexcitation, the initially formed LMCT excited state undergoes rapid intersystem crossing and subsequently decays within approximately 30 ps to generate a long-lived reactive triplet state, commonly denoted wO. This active triplet species has a lifetime of 55 ± 20 ns and a quantum yield of approximately 0.6 [6, 9]. Owing to its pronounced oxygen-centered radical character and high electrophilicity, wO is a strongly oxidizing species that engages substrates through two principal and interconnected reactivity modes: single-electron transfer (SET) and hydrogen-atom transfer (HAT). These pathways are governed by substrate-dependent thermodynamic and kinetic factors, including oxidation potential, C–H bond dissociation energy, polarity matching, and steric accessibility, with the latter often playing a decisive role in determining site selectivity in HAT processes [9, 10, 39, 46].

With an estimated excited-state reduction potential of approximately +2.44 V versus SCE for the $[W_{10}O_{32}]^{4-*}/[W_{10}O_{32}]^{5-}$ couple

(Scheme 2) [9], the decatungstate can oxidize a broad range of electron-rich and redox-active substrates. The thermodynamic feasibility of catalyst regeneration is governed by the ground-state reduction potential of the $[W_{10}O_{32}]^{4-}/[W_{10}O_{32}]^{5-}$ couple ($E = -0.97$ V vs. SCE) [44], with regeneration pathways involving back-electron transfer or oxidation by external terminal oxidants. The one-electron-reduced species $[W_{10}O_{32}]^{5-}$ can further participate in redox equilibria, including disproportionation processes that regenerate $[W_{10}O_{32}]^{4-}$ alongside more reduced species such as $[W_{10}O_{32}]^{6-}$. The latter is a potent reductant, with a half-wave reduction potential of $E_{1/2,red}([W_{10}O_{32}]^{5-}/[W_{10}O_{32}]^{6-}) = -1.48$ V versus SCE in acetonitrile [56]. Collectively, these coupled processes establish a dynamic redox network that is particularly relevant to dual catalytic systems [57–60], where controlled electron and radical fluxes are essential for productive reactivity.

In this regard, it is worth mentioning that the electronic structure and redox behavior of the decatungstate have been extensively investigated using combined experimental and computational approaches. Bagno, Ravelli, and coworkers employed density functional theory (DFT), UV–vis spectroscopy, and electron paramagnetic resonance (EPR) to characterize photogenerated reduced species [9, 61]. These studies provide a molecular-level description of the accessible redox landscape and demonstrate that electronic delocalization across the polyoxotungstate framework enables reversible multielectron redox processes while preserving the characteristic structural integrity of the cluster, thereby underpinning the exceptional catalytic robustness of the system.

In the SET regime, substrates with sufficiently low oxidation potentials undergo outer-sphere electron transfer to excited decatungstate, generating radical cations that can subsequently undergo deprotonation, fragmentation, or further radical transformations (Scheme 2, left) [62–65]. In parallel, HAT represents the dominant pathway in decatungstate-mediated C–H functionalization. In this regime, electrophilic excited-state oxo ligands directly abstract a hydrogen atom from the substrate, generating a carbon-centered radical and the one-electron-reduced catalyst (Scheme 2, right). Reactivity is primarily governed by polarity matching between the excited state and the C–H bond, together with favorable HAT thermodynamics, enabling the activation of both relatively weak C–H bonds, such as benzylic, allylic, and α -heteroatom C–H bonds, and strong aliphatic C–H bonds. The resulting carbon-centered radicals serve as key intermediates



SCHEME 2 | Mechanistic pathways for decatungstate photocatalysis.

in downstream bond-forming processes, including radical addition, cyclization, and cross-coupling.

4 | Ion Pairing, Counterion Stability, and Electrostatic Effects

In solution, the decatungstate exists as an ion-paired assembly with its counterions, with the extent of association governed by counterion identity and solvent polarity [23, 38]. Depending on the dielectric constant of the medium, these ion pairs span a continuum from tightly associated contact ion pairs to more dissociated, solvent-separated species, consistent with established electrolyte behavior [23, 66].

In contrast to many photoredox and energy-transfer systems, where ion pairing can significantly alter excited-state lifetimes and redox properties [11, 12, 14, 66], experimental studies on the decatungstate suggest that the intrinsic photophysical properties of the $[W_{10}O_{32}]^{4-}$ core are largely preserved across different counterions [9, 22]. In particular, ligand-to-metal charge-transfer (LMCT) excitation and the resulting triplet-state reactivity appear to be only minimally affected by counterion variation, while the fundamental thermodynamics of hydrogen-atom abstraction remain essentially unchanged. Instead, counterion identity primarily influences solution-phase organization, including solubility, dispersion behavior, aggregation state, and substrate accessibility to the polyoxometalate core. These parameters govern the efficiency of substrate-catalyst encounters and the rate of productive radical formation, particularly in systems requiring continuous radical generation, such as dual catalytic manifolds, radical chain processes, or transformations operating under steady-state radical flux conditions. Accordingly, ion pairing may indirectly modulate reactivity by controlling the formation kinetics and effective concentration of reactive intermediates, thereby affecting the overall catalytic efficiency and selectivity [22, 23, 66]. Thus, variations in counterion identity can determine how effectively the catalytic species engage substrates in solution, not by altering the intrinsic excited-state reactivity of the decatungstate core but by regulating its availability and interaction dynamics within the reaction medium.

Beyond the catalyst-counterion association, electrostatic interactions can also arise directly between the anionic decatungstate photocatalyst and charged substrates. Recent studies have demonstrated that attractive interactions between the decatungstate and positively charged substrates can influence catalyst-substrate organization in solution, with significant consequences for both HAT kinetics and site selectivity. For instance, Britton and coworkers demonstrated that protonated ammonium-containing substrates undergo substantially accelerated decatungstate-catalyzed $C(sp^3)$ -H fluorination as a result of attractive electrostatic interactions between the cationic substrate and anionic catalyst, promoting the formation of a catalyst-substrate precursor complex prior to hydrogen-atom transfer [67]. Transient absorption spectroscopy and kinetic studies showed that these interactions increase the rate of HAT without significantly altering the intrinsic photophysical properties of the decatungstate excited state, thereby establishing electrostatic preorganization as a distinct mechanistic contribution beyond the well-established steric and polar effects governing the decatungstate HAT selectivity. Building on this concept, Kuninobu, Torigoe, and

coworkers subsequently exploited electrostatic attraction between protonated ammonium substrates and the anionic decatungstate photocatalyst to direct site-selective $C(sp^3)$ -H alkylation [68]. In these systems, the catalyst-substrate association enabled selective benzylic $C(sp^3)$ -H alkylation adjacent to the ammonium group, a selectivity that cannot be explained solely by bond dissociation energies or steric accessibility. This strategy was subsequently extended to peptide modification, where electrostatic interactions enabled selective alkylation of valine residues positioned near the N-terminus and facilitated the late-stage functionalization of structurally complex peptides [69]. Collectively, these studies demonstrate that electrostatic catalyst-substrate interactions provide an additional level of control over decatungstate photocatalysis by influencing both reaction kinetics and site selectivity, thereby extending the mechanistic framework beyond conventional considerations of steric effects and polarity matching.

Beyond influencing solution-phase organization, the intrinsic chemical stability of the counterion itself represents an additional factor governing catalyst performance under photocatalytic conditions (see also Section 4.4). Early mechanistic investigations by Yamase and coworkers revealed that tetraalkylammonium counterions are susceptible to oxidation by photoexcited decatungstate, resulting in gradual counterion decomposition through hydrogen abstraction and subsequent formation of alkene by-products such as 1-butene [19]. Systematic studies comparing tetramethyl-, tetrapropyl-, tetrabutyl-, and tetrahexylammonium decatungstate salts further demonstrated that susceptibility to counterion oxidation increases with alkyl chain length, leading to greater competition between the counterion and substrate for productive hydrogen-atom transfer and a corresponding decrease in catalytic efficiency [20]. These findings establish that the counterion is not merely a charge-balancing species but can actively participate in the photocatalytic process, thereby influencing catalyst stability and reaction efficiency, particularly under prolonged irradiation.

The reaction medium itself may also participate in decatungstate photocatalysis under specific conditions. Acetonitrile is relatively resistant to hydrogen-atom abstraction by photoexcited decatungstate because of unfavorable polar effects and is therefore widely employed as a solvent for decatungstate photocatalysis [6, 70]. Nevertheless, hydrogen-atom abstraction from MeCN occurs with a low but measurable second-order rate constant ($k_H = 6.5 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$), indicating that solvent activation may become relevant for poorly reactive substrates or under conditions in which productive substrate HAT is intrinsically slow [6, 70].

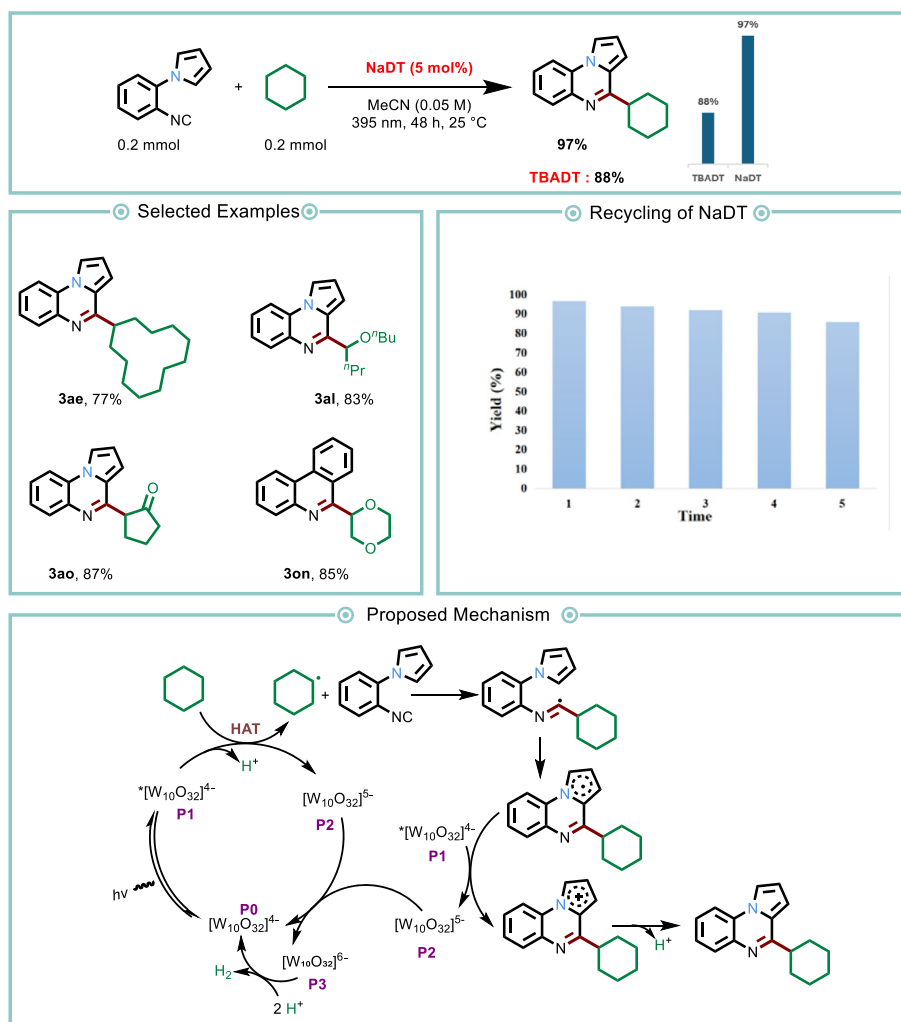
Collectively, these studies demonstrate that counterion identity can influence decatungstate photocatalysis through multiple interconnected factors, including ion pairing, counterion chemical stability, and electrostatic interactions that govern catalyst-substrate organization. More broadly, the reaction medium can further modulate these interactions and, under appropriate conditions, become a competing participant in HAT reactivity. While the trends discussed throughout this review are consistent with counterion-dependent effects, direct spectroscopic evidence correlating ion-pair structure and catalyst-substrate association with catalytic performance in decatungstate photocatalysis remains limited, highlighting an important area for future mechanistic investigation.

4.1 | Counterion-Dependent Reactivity in Homogeneous and Heterogeneous Systems—Comparative Reactivity of NaDT and TBADT

Among the various decatungstate salts employed in hydrogen-atom-transfer (HAT) photocatalysis, sodium decatungstate (NaDT) and tetrabutylammonium decatungstate (TBADT) represent the two most extensively studied systems [1, 2, 6, 8]. Although both catalysts share the identical photoactive $[W_{10}O_{32}]^{4-}$ core with comparable excited-state properties, they often display distinct reactivity profiles under otherwise comparable reaction conditions, underscoring the influence of the counteranion on the catalytic performance. Across a broad range of C–H functionalization reactions, NaDT frequently exhibits efficiency comparable to, or in most cases exceeding, that of TBADT, particularly in reaction systems that require heterogeneous or multiphase conditions, mixed-solvent environments, and cooperative dual catalytic manifolds for effective formation of the desired products in high yield. Representative transformations include radical cascade cyclizations, oxyfunctionalizations, trifluoromethylthiolations, and transition-metal-coupled processes [71–76].

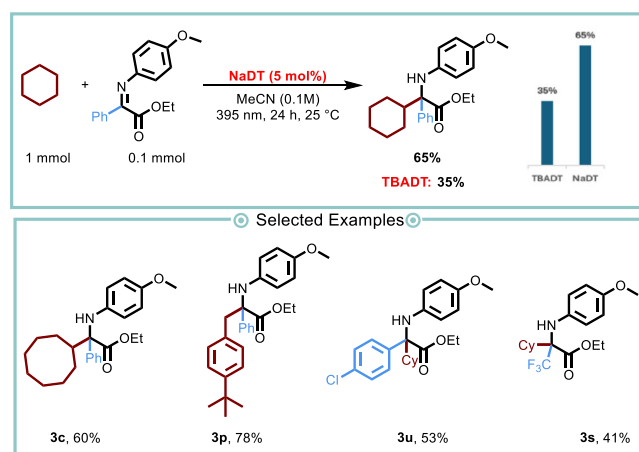
A representative example is provided by He and coworkers in decatungstate-catalyzed radical cascade alkylation/cyclization reactions, where NaDT delivers a higher efficiency than TBADT in the coupling of 1-(2-isocyanophenyl)-1H-pyrrole with cyclohexane (Scheme 3) [71]. The reaction proceeds through a sequence of hydrogen-atom abstraction, radical addition to the isocyanide carbon, intramolecular cyclization, and subsequent oxidation and deprotonation steps, leading to the formation of the alkylated fused heterocyclic product.

Importantly, since both catalysts operate through the same decatungstate-mediated hydrogen-atom-transfer pathway, the observed differences are unlikely to arise from changes in the intrinsic excited-state properties of the $[W_{10}O_{32}]^{4-}$ core. Instead, a key distinction between NaDT and TBADT lies in their phase behavior in polar organic solvents, such as acetonitrile. TBADT is readily soluble in such media, forming a fully homogeneous reaction system in which the decatungstate anion is molecularly dispersed. In contrast, NaDT exhibits limited solubility and often operates under heterogeneous or colloidal conditions. This difference in phase behavior does not alter the photochemical reactivity of the decatungstate core; however, it



SCHEME 3 | Radical cascade alkylation/cyclization of isocyanides with simple alkanes, ethers, and ketones. The recycling of NaDT graph is reproduced from ref. [71], under the Creative Commons Attribution–NonCommercial–NoDerivatives 4.0 License (CC BY-NC-ND 4.0).

may influence the catalyst–substrate interface and modulate the kinetics of radical processes, including hydrogen-atom abstraction and subsequent radical transformations, ultimately affecting product formation. Notably, the additional advantage of NaDT in this catalytic system also lies in its practical operational benefits. In acetonitrile, NaDT can be readily recovered by centrifugation and reused over multiple catalytic cycles without a significant loss of activity. This recyclability provides important sustainability and economic benefits, particularly given the cost of decatungstate catalysts. In contrast, TBADT, being fully soluble in polar solvents, is generally not recoverable under standard reaction conditions. Accordingly, NaDT represents a promising alternative for more sustainable and scalable HAT-based photocatalytic applications.

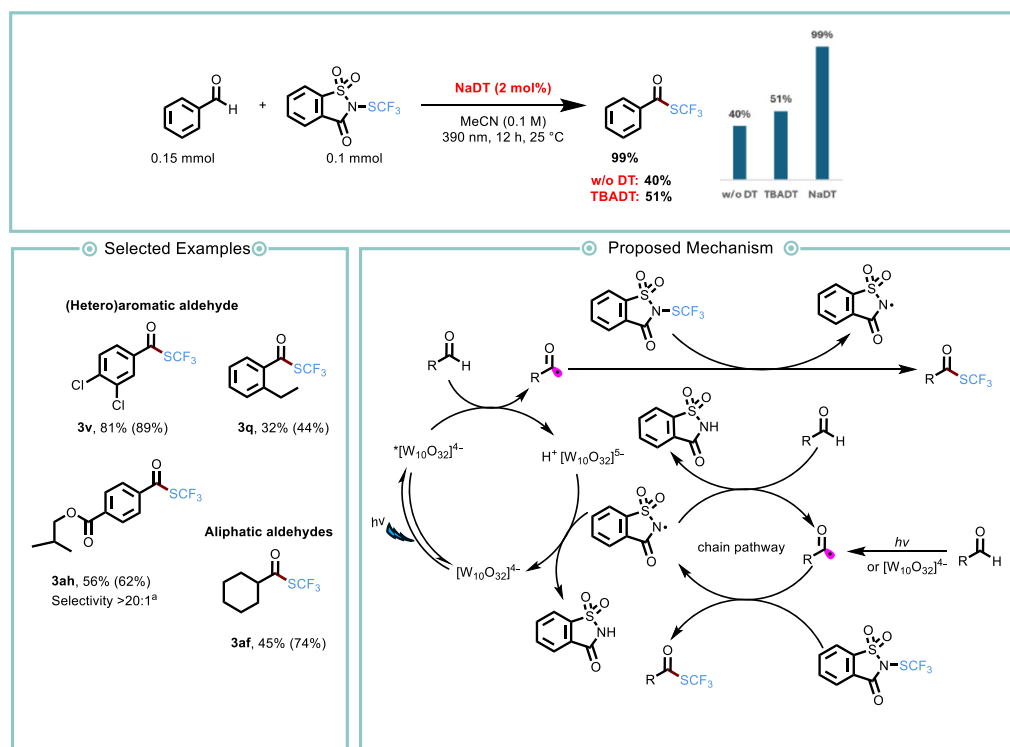


SCHEME 4 | Decatungstate photocatalyzed C–H alkylation of α -aryl α -*N*-protected imino esters [72].

A similar enhancement in reactivity with NaDT is observed in the C–H alkylation of α -aryl, *N*-protected imino esters toward α,α -disubstituted amino acid derivatives (Scheme 4) [72]. Under identical reaction conditions, NaDT delivers significantly higher yields (65%) compared to those of TBADT (35%). Notably, the addition of crown ethers to increase the solubility of NaDT does not improve the reaction outcome, suggesting that the catalytic performance is not governed by bulk solubility alone. These observations indicate that factors beyond simple solubility differences contribute to the distinct reactivity profiles of the two catalytic systems.

A similar divergence in reactivity is observed in visible-light-induced trifluoromethylthiolation reactions reported by Yuan, Gao, Britton, and coworkers, where sodium decatungstate (NaDT) affords near-quantitative yields (99%), whereas tetrabutylammonium decatungstate (TBADT) shows significantly lower efficiency (51%) under identical conditions (Scheme 5) [73]. Notably, product formation is also observed in the absence of a decatungstate catalyst, delivering yields of up to 40%, which was attributed to a radical chain propagation pathway involving the *N*-trifluoromethylthiosaccharin reagent. Mechanistic studies suggest that, in this system, the decatungstate serves as an efficient radical initiator and regulator of the steady-state concentration of reactive intermediates. Within this framework, the higher efficiency observed with NaDT indicates that counterion identity can influence the efficiency of radical initiation and the sustained formation of reactive intermediates, even in systems where chain propagation contributes significantly to the overall product formation.

The counterion-dependent behavior is further evident in the oxidative C–H functionalization of aliphatic amines. In the selective



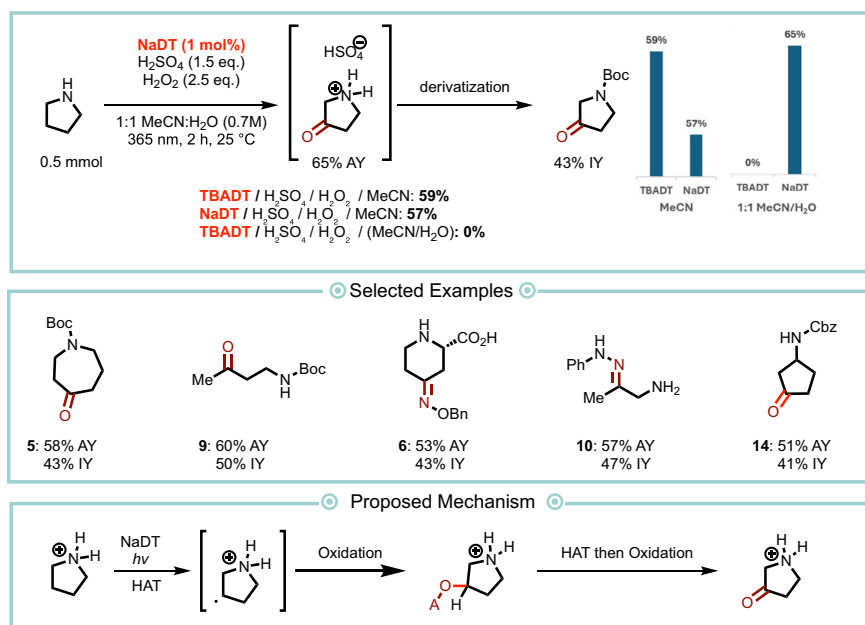
SCHEME 5 | Synthesis of trifluoromethylthioesters from aldehydes [73].

oxyfunctionalization reported by Schultz and coworkers, sodium decatungstate (NaDT) and tetrabutylammonium decatungstate (TBADT) exhibit comparable reactivity in acetonitrile for the conversion of pyrrolidine to pyrrolidin-3-one, whereas a pronounced divergence in catalytic performance is observed in mixed aqueous–organic media (Scheme 6) [74]. Under these conditions, NaDT shows a significantly enhanced efficiency, while TBADT displays no observable product formation. This behavior reflects two interrelated factors. First, chemoselectivity is governed by protonation-controlled hydrogen-atom transfer, in which amine protonation suppresses competing N–H abstraction and directs reactivity toward remote β - or γ -C–H bonds. Second, catalytic efficiency depends strongly on catalyst–medium compatibility, where NaDT likely benefits from favorable solvation and ion-pair stabilization in polar and protic environments that support substrate access and productive turnover. In contrast, the tetrabutylammonium counterion is poorly accommodated in aqueous media, leading to disrupted solvation and reduced accessibility of the catalytically active species, ultimately suppressing reactivity under otherwise identical conditions.

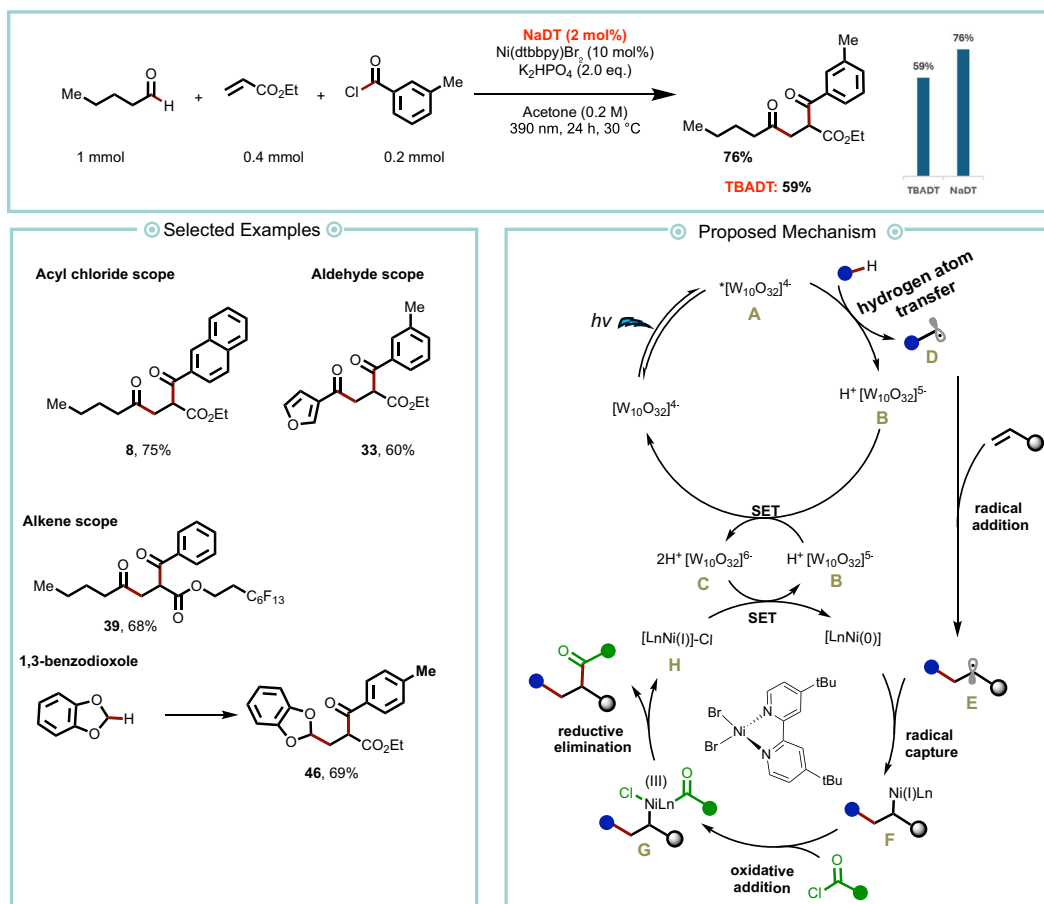
The influence of counterion identity extends beyond single-component systems to more complex dual-catalytic transformations. In 2022, Ackermann and Wang reported a nickel/decatungstate dual catalytic system enabling the three-component carboacylation of unactivated alkenes, merging C–C bond formation and acylation in a single step (Scheme 7) [75]. In the optimized model reaction, sodium decatungstate (NaDT) affords the desired product in a 76% yield, whereas replacement with tetrabutylammonium decatungstate (TBADT) decreases the yield to 59%. Mechanistically, the reaction proceeds via decatungstate-mediated hydrogen-atom abstraction to generate a carbon-centered radical, which adds to the alkene to form a radical intermediate that is subsequently intercepted by the nickel catalyst, delivering the carboacylated product through a cross-coupling sequence. In this manifold, efficient turnover relies on the maintenance of a steady and kinetically matched

radical flux, synchronized with inter-catalyst communication between the photoredox and nickel cycles. NaDT provides a more favorable balance for orchestrating these coupled processes than TBADT, thereby delivering a higher yield of the desired product.

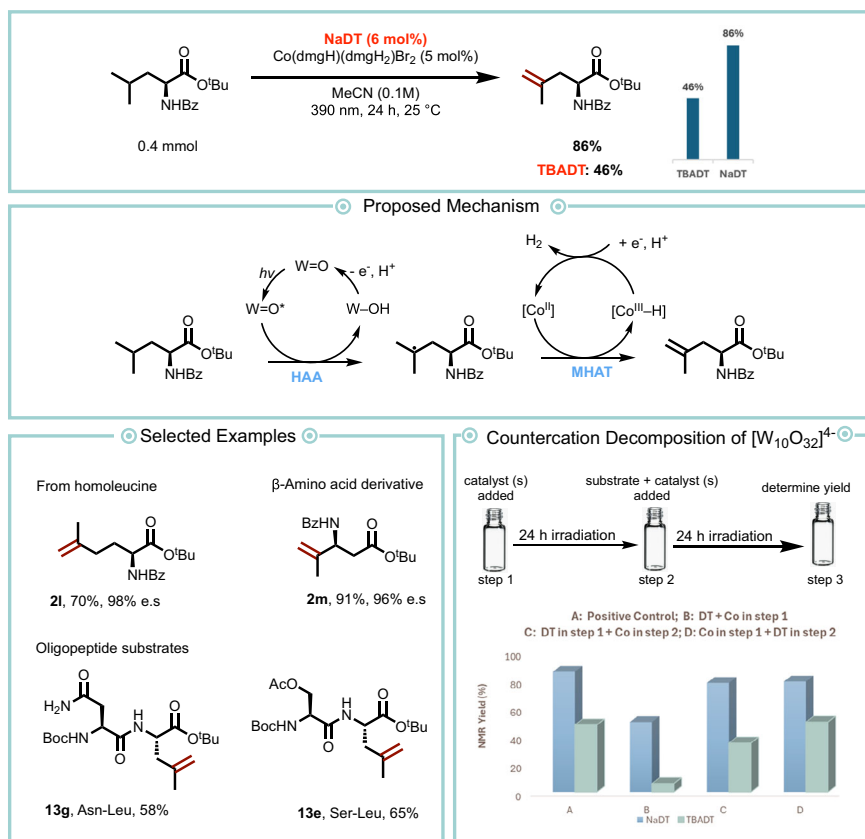
The influence of counterion identity becomes particularly pronounced in complex dual catalytic systems involving redox-active co-catalysts. In 2024, Wendlandt and coworkers reported a visible-light-driven, terminal-selective acceptorless dehydrogenation of aliphatic amino acids and peptides using a decatungstate/cobaloxime dual catalytic system (Scheme 8) [76]. In the model reaction, sodium decatungstate (NaDT) affords the γ,δ -dehydrogenated product in 86% yield, whereas tetrabutylammonium decatungstate (TBADT) delivers only 46% under identical conditions, highlighting a substantial counterion-dependent difference in the catalytic performance. Mechanistically, the transformation proceeds via decatungstate-mediated hydrogen-atom abstraction to generate a carbon-centered radical, which is intercepted by the cobaloxime co-catalyst through a metal-mediated hydrogen evolution pathway. Time course and control experiments indicate that counterion identity influences two key aspects of catalytic behavior. First, catalyst stability under photochemical conditions is strongly counterion dependent. While TBADT is relatively stable in the absence of the co-catalyst, the presence of cobaloxime accelerates degradation pathways associated with the tetrabutylammonium counterion, including the formation of 1-butene and rapid loss of catalytic activity. Notably, the formation of 1-butene from TBADT under irradiation was first reported by Yamase and coworkers [19]. Under full catalytic conditions, this leads to incomplete substrate conversion, whereas NaDT maintains catalytic integrity and enables sustained turnover. Second, the timing of co-catalyst addition further highlights this effect: early addition results in significant yield erosion, particularly in the TBADT system, consistent with accelerated deactivation pathways, whereas delayed addition improves performance in both cases while preserving the higher efficiency of NaDT. Collectively, these findings demonstrate that



SCHEME 6 | Oxyfunctionalization of aliphatic Amines. AY: Assay yields; IY: Isolated yield of derivatized products. The reaction with TBADT was carried out by high-throughput experimentation (HTE) with 2.5 mol% of TBADT, while an integrated photoreactor was used for the NaDT [74].



SCHEME 7 | Nickel/decatungstate photocatalyzed carbocarbonylation of alkenes [75].



SCHEME 8 | Decatungstate-catalyzed synthesis of terminal alkenes [76].

the inorganic Na^+ counterion provides enhanced robustness and compatibility in redox-active dual-catalytic environments. They further establish counterion stability and catalyst-co-catalyst compatibility as key determinants of performance in decatungstate-mediated transformations.

4.2 | TBADT-Favored Systems

As discussed in the previous section, although sodium decatungstate (NaDT) often exhibits comparable or superior performance in hydrogen-atom-transfer (HAT) photocatalysis, a subset of reaction manifolds displays a clear preference for tetrabutylammonium decatungstate (TBADT). These cases highlight that counterion effects in decatungstate chemistry are not inherently directional but instead arise from a balance between ion-pair structure, solvation behavior, and the kinetic requirements of radical turnover. In particular, TBADT is advantageous in systems requiring a fully homogeneous reaction medium, rapid diffusion of transient radical species, and efficient chain propagation processes.

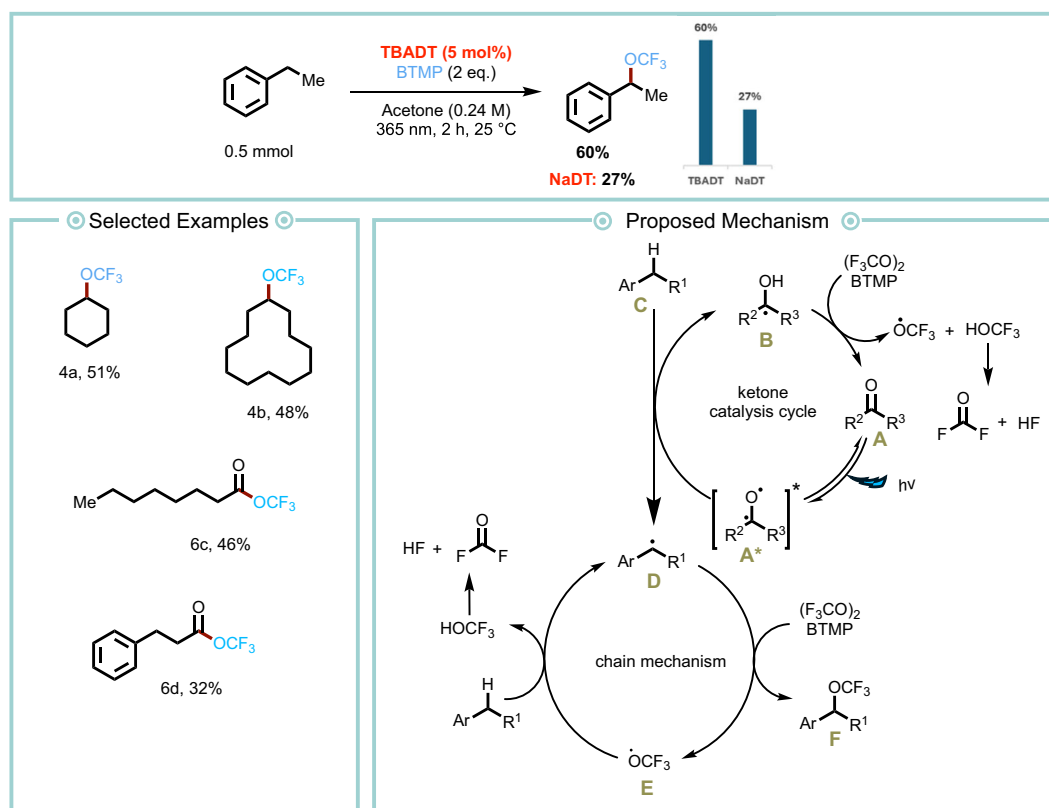
A representative example is the C–H trifluoromethoxylation of unactivated substrates reported by Riedel, Christmann, and coworkers, in which bis(trifluoromethyl) peroxide (BTMP) serves as the OCF_3 radical precursor (Scheme 9) [77]. Under optimized conditions, TBADT significantly outperforms NaDT in the functionalization of ethylbenzene (60% vs. 27%). Mechanistic studies suggest that the reaction proceeds through a hybrid regime combining photocatalytic initiation with self-propagating radical chain chemistry. The observed quantum yield ($\Phi > 9$) indicates that radical chain propagation contributes significantly to product

formation, suggesting that overall reaction efficiency depends on both photochemical radical initiation and the ability to sustain a steady-state concentration of reactive radical intermediates. Gravimetric and kinetic analyses further indicate that BTMP exhibits higher solubility in acetone than in acetonitrile, increasing radical availability and facilitating more efficient chain propagation. Notably, productive trifluoromethoxylation can proceed even in the absence of the decatungstate, consistent with BTMP-derived species sustaining chain propagation, while the decatungstate primarily assists radical generation for less reactive substrates.

Within this framework, TBADT is well suited to homogeneous radical networks. Its generally high solubility in polar organic solvents ensures molecular dispersion of the ion-paired $[\text{W}_{10}\text{O}_{32}]^{4-}$ species, enabling efficient interaction with radical precursors during initiation and turnover. This uniform distribution supports sustained radical generation and a stable reactive pool. By contrast, NaDT exhibits limited solubility in the same media and a greater tendency toward aggregation or partial phase separation. Under these conditions, reduced dispersion of the active decatungstate species may contribute to a lower initiation efficiency, which in chain-propagating systems can translate into a pronounced decrease in overall reaction yield.

4.3 | Condition-Dependent/Interchangeable Systems

In a number of decatungstate-mediated hydrogen-atom-transfer (HAT) transformations, the relative performance of sodium decatungstate (NaDT) and tetrabutylammonium decatungstate



SCHEME 9 | C–H trifluoromethoxylation of non-activated methylene $\text{C}(\text{sp}^3)\text{--H}$ and formyl $\text{C}(\text{sp}^2)\text{--H}$ bonds [77].

(TBADT) is not an intrinsic property of the catalyst but instead depends strongly on the surrounding reaction environment. In these systems, both salts function as competent photocatalysts, and the preferred counterion emerges from a balance between solvent effects, additives, co-catalysts, and the underlying reaction mechanism. Such examples highlight that counterion effects in decatungstate photocatalysis are often condition-dependent rather than universally directional.

A representative example is the contra-thermodynamic alkene isomerization reported by Wendlandt and coworkers, in which both NaDT and TBADT catalyze the transformation efficiently but display solvent-dependent performance (Scheme 10) [78]. The reaction proceeds through a dual catalytic manifold in which photoexcited decatungstate initiates hydrogen-atom abstraction to generate a carbon-centered radical, while a cobaloxime co-catalyst mediates formal alkene isomerization. A hydrogen-atom shuttle, 2,4,6-triisopropylbenzene disulfide (TripS-S), facilitates hydrogen transfer during radical termination, enabling efficient catalytic turnover.

Under otherwise comparable conditions, the relative performance of the two salts is reversed depending on the solvent choice. In acetonitrile, TBADT affords slightly higher yields in the isomerization of 1-(2-methyl-1-propenyl)-4-phenoxybenzene (76% vs. 69% for NaDT), whereas in acetone, NaDT becomes the more effective catalyst (96% vs. 82%). These trends indicate that subtle changes in the solvent environment can shift the balance between ion pairing, solvation, and catalyst participation within the multi-component catalytic network, ultimately affecting the overall efficiency.

Further evidence for this sensitivity to reaction conditions is provided by the related decatungstate/cobaloxime-catalyzed dehydrogenation of aliphatic amino acids and peptides (cf. Scheme 8) [76]. Although mechanistically related, this transformation exhibits a distinct counterion dependence compared to the alkene isomerization system and is performed in the absence of the hydrogen-atom shuttle TripS-S, highlighting how additive composition can significantly alter the operative catalytic regime. Taken together, these

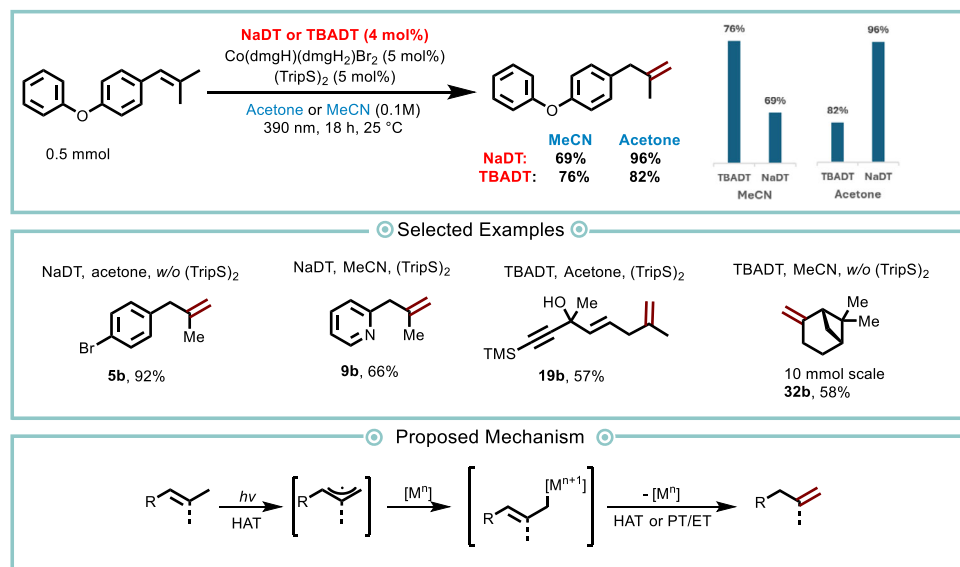
studies demonstrate that counterion effects in decatungstate photocatalysis cannot be understood in isolation but must be interpreted in the context of solvent, additives, and co-catalyst architecture, which together define the effective catalytic environment.

4.4 | Phosphonium Counterions: Reactivity and Durability

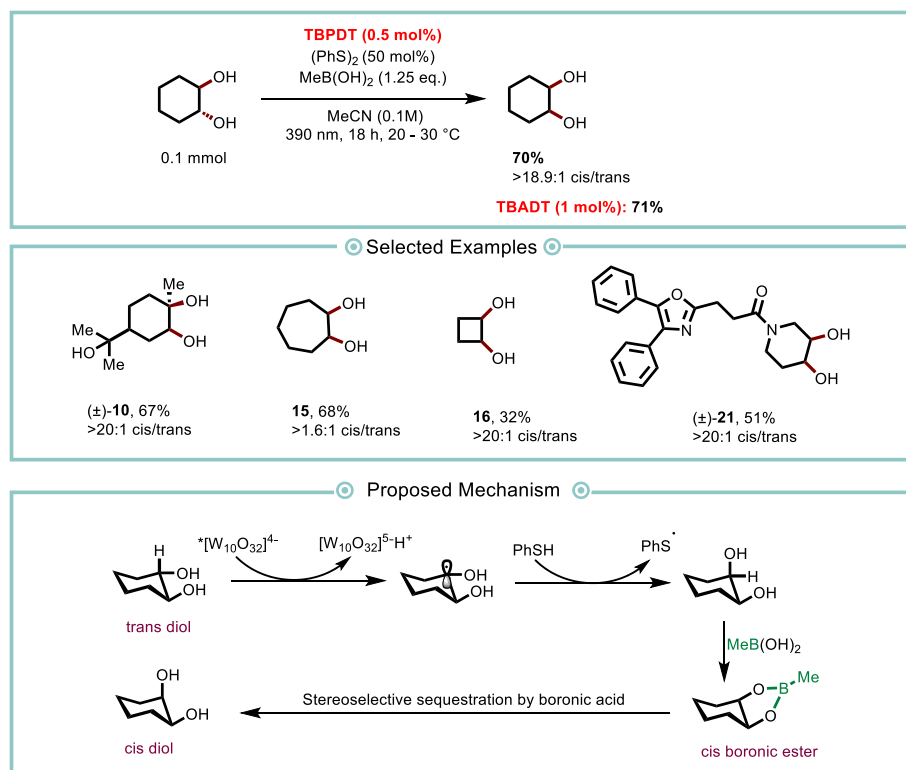
Beyond conventional alkali metal and tetraalkylammonium salts, recent studies have explored alternative organic counterions in decatungstate photocatalysis. Among these, phosphonium-based decatungstate salts have emerged as systems with distinct solubility characteristics and catalytic behavior compared with those of their ammonium analogs.

This is exemplified by the light-driven contra-thermodynamic epimerization of trans-diols reported by MacMillan, Oswood, and coworkers, which combines hydrogen-atom-transfer (HAT) photocatalysis with boronic acid-mediated transient thermodynamic control (Scheme 11) [79]. In this system, tetrabutylammonium decatungstate (TBADT) and tetrabutylphosphonium decatungstate (TBPDT) afforded comparable yields of the cis-boronic ester (71% vs. 70%). However, TBPDT achieved this outcome at half the catalyst loading (0.5 mol% vs. 1 mol%), indicating enhanced catalytic efficiency under otherwise identical conditions. This improvement was attributed primarily to the higher solubility of the phosphonium salt in acetonitrile, which facilitates more effective catalyst dispersion and substrate accessibility. Mechanistically, the reaction proceeds through photoexcitation of the decatungstate, followed by hydrogen-atom abstraction from the α -oxy C–H bond of the diol to generate a carbon-centered radical, which is subsequently quenched by diphenyl disulfide, thereby regenerating the catalyst. In the presence of methylboronic acid, selective trapping of the cis-diol as a thermodynamically favored boronic ester drives the overall contra-thermodynamic transformation (Scheme 11).

Beyond differences in the catalytic efficiency, phosphonium counterions can also broaden the operational scope of



SCHEME 10 | Contra-thermodynamic positional isomerization of various internal alkenes [78].

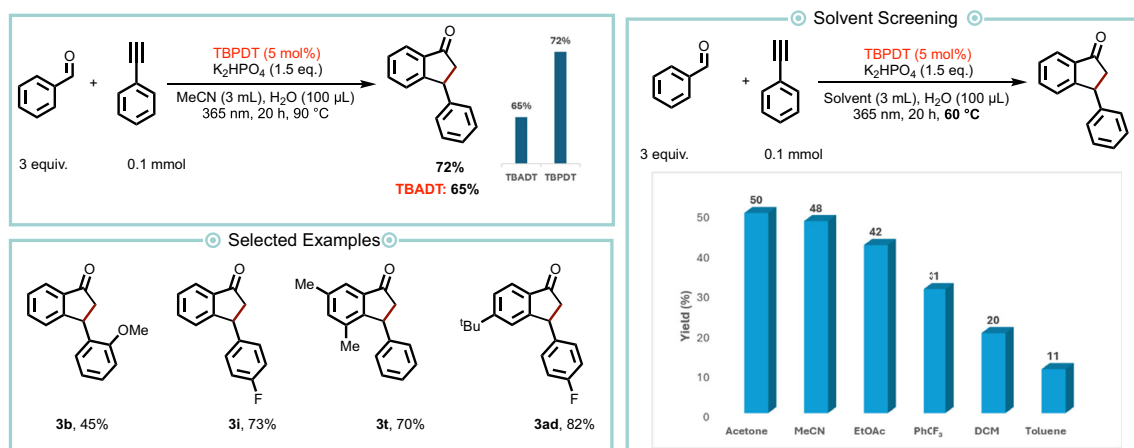


SCHEME 11 | Selective epimerization of cyclic diols via HAT and boronic acid [79].

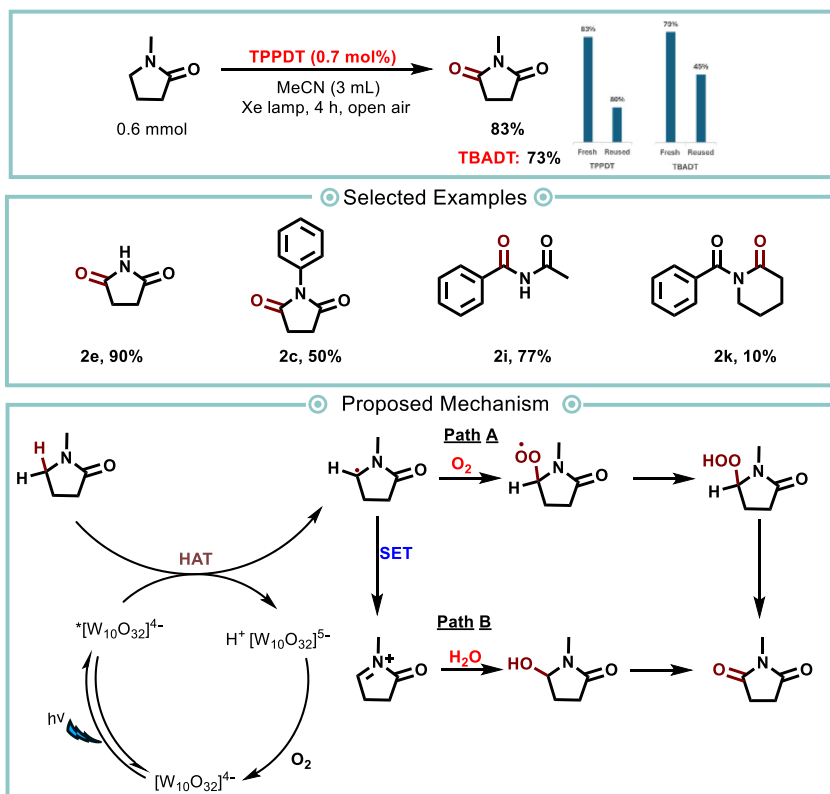
decatungstate photocatalysis. In our recent C–H annulation of aromatic aldehydes with terminal alkynes, tetrabutylphosphonium decatungstate (TBPD) afforded higher yields than TBADT under identical conditions (72% vs. 65%) (Scheme 12) [80]. More notably, TBPD maintained high catalytic activity across a broader range of solvents, including trifluorotoluene, ethyl acetate, and dichloromethane, whereas conventional ammonium-based systems typically exhibited reduced performance because of limited solubility or catalyst aggregation.

The use of tetraarylphosphonium counterions provides further evidence for the importance of counterion identity in determining the stability and performance of decatungstate photocatalysts. This is exemplified by the development of tetraphenylphosphonium

decatungstate (TPPD) for the aerobic α-oxygenation of amides to imides [81]. In contrast to conventional tetraalkylammonium decatungstate salts, whose aliphatic C–H bonds are susceptible to hydrogen-atom abstraction under prolonged irradiation [19, 20], replacement with a tetraphenylphosphonium counterion substantially enhances resistance to counterion oxidation because of the higher bond dissociation energies of its aromatic C–H bonds [81]. Although TPPD afforded only a modest increase in product yield compared with that of TBADT (83% vs. 73%), the most significant distinction between the two catalysts was their stability and recyclability (Scheme 13). TPPD could be readily recovered after the reaction, and ¹H NMR, ³¹P NMR, IR spectroscopy, and ESI-MS confirmed the preservation of both the tetraphenylphosphonium counterion and the decatungstate framework.



SCHEME 12 | Decatungstate photocatalyzed C–H annulation for the synthesis of indanones derivatives [80].



SCHEME 13 | Tetraphenylphosphonium decatungstate (TPPDT)-catalyzed aerobic α -oxygenation of amides to imides [81].

In contrast, TBADT could not be recovered using the same procedure because the catalyst formed a sticky residue, while ^1H NMR analysis of the post-reaction solution showed complete disappearance of the tetrabutylammonium alkyl signals, confirming degradation of the TBA counterion under the photocatalytic conditions. Importantly, the recovered TPPDT retained high catalytic activity upon reuse, affording the corresponding imide in an 80% yield. This study further demonstrates that rational counterion engineering can be employed not only to modulate catalyst solubility and ion-pairing behavior but also to improve catalyst durability and recyclability, thereby extending the catalyst lifetime under prolonged photocatalytic conditions.

4.5 | Decatungstate-Based Ionic Liquids: Toward a Solvent-in-Catalyst Regime

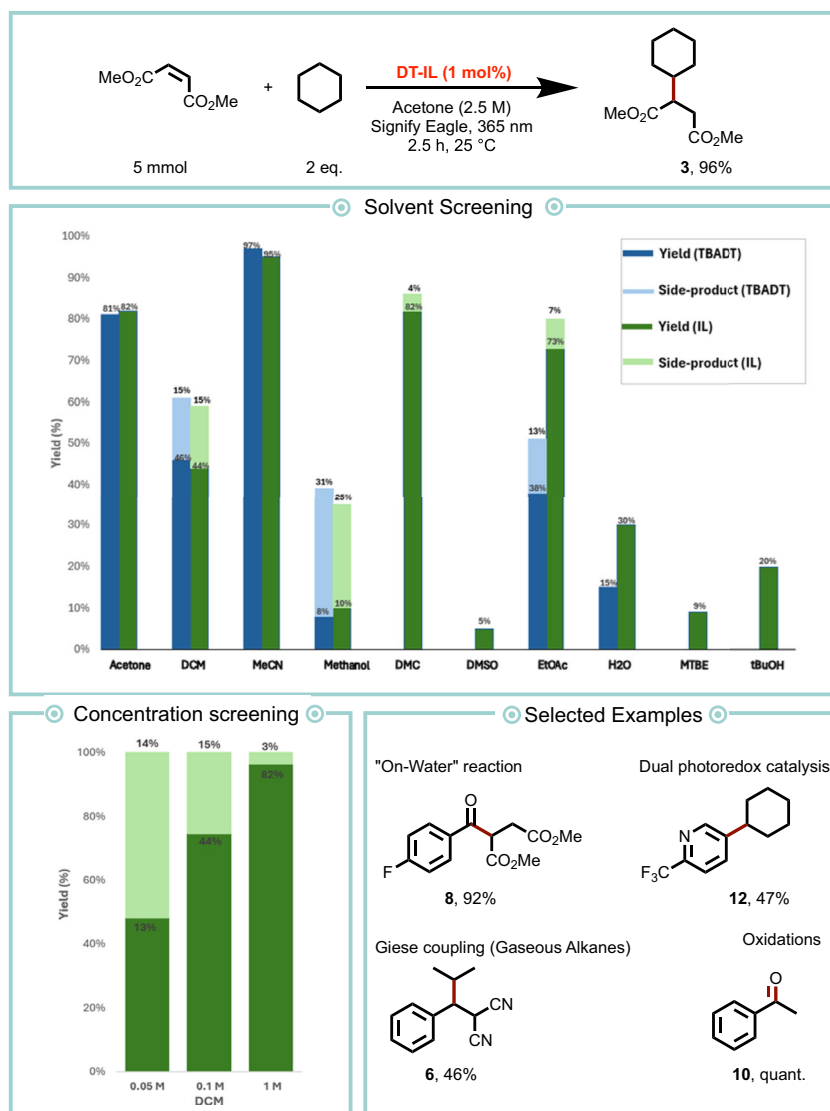
Beyond simple counterion substitution, efforts to improve the practicality and versatility of decatungstate photocatalysis have led to the development of ionic-liquid-based systems. Noël and coworkers [82] reported a decatungstate-based ionic liquid (DT-IL) formed by pairing the $[W_{10}O_{32}]^{4-}$ anion with a trihexyltetradecylphosphonium cation. Spectroscopic characterization by IR, ^{31}P NMR, and UV-vis spectroscopy confirmed that the polyoxyometalate structure and photophysical properties of decatungstate are retained in the ionic liquid form.

The photocatalytic performance of DT-IL was benchmarked against TBADT in a Giese-type coupling between cyclohexane and dimethyl maleate (Scheme 14), where both catalysts deliver comparable yields and reaction rates. However, DT-IL exhibits

significantly broader solvent compatibility, maintaining moderate to high catalytic activity in solvents such as dichloromethane, dimethyl carbonate, ethyl acetate, and even water. In contrast, reduced reactivity is observed in methanol, ethanol, dimethyl sulfoxide, and methyl *tert*-butyl ether, underscoring the sensitivity of conventional TBADT systems to solvent coordination and medium effects. This expanded solvent tolerance addresses a key limitation of traditional decatungstate salts and highlights the advantage of integrating the catalytic anion directly into an ionic-liquid framework.

In addition, owing to its enhanced solubility, DT-IL tolerates substantially higher catalyst loadings and can be operated under near-neutral conditions. In the Giese reaction, increasing both catalyst and substrate concentrations suppresses competing solvent-activation pathways observed under dilute conditions, resulting in improved selectivity and productivity (Scheme 14). These observations indicate that counterion identity can influence photocatalytic performance not only through solubility effects but also by modulating the effective reaction environment, including local concentration, solvation dynamics, and competing reaction pathways.

The versatility of DT-IL is further demonstrated across a broad range of transformations, including hydroacylation under “on-water” conditions, photochemical oxidations, Minisci-type alkylations, nickel dual catalytic systems, and Giese couplings involving gaseous alkanes. Importantly, the catalyst can be readily recovered by simple phase separation and reused without a significant loss of activity, thereby avoiding chromatographic purification and substantially reducing solvent consumption.



SCHEME 14 | Photocatalytic performance of DT-IL. The solvent screening graph is adapted from ref. [82]. under the Creative Commons Attribution 3.0 License (CC BY 3.0).

From the perspective of counterion effects, DT-IL systems occupy a distinct position within the decatungstate family. Whereas NaDT, TBADT, and related phosphonium decatungstate salts primarily differ in solubility and ion-pairing behavior, ionic-liquid formulations integrate the counterion as an intrinsic component of the reaction medium. As a result, key parameters such as catalyst solubility, solvent compatibility, accessible catalyst concentration, and ease of recovery are directly governed by the counterion identity. The DT-IL platform thus illustrates how counterion selection can extend beyond modulation of ion pairing to influence the practical implementation of decatungstate photocatalysis across diverse reaction classes and operating conditions.

4.6 | Immobilized Decatungstate (Heterogeneous Systems)

Immobilization of decatungstate on solid supports extends counterion-dependent behavior into heterogeneous photocatalysis, enabling the development of more robust and recyclable

catalytic systems. The importance of counterion identity in heterogeneous decatungstate photocatalysis was recognized in early studies of silica-supported decatungstate catalysts. By systematically comparing tetraalkylammonium and sodium decatungstate salts immobilized on silica, Maldotti and coworkers demonstrated that the counterion can modulate the local surface polarity surrounding the photoactive decatungstate cluster, thereby influencing substrate accessibility and photocatalytic efficiency [24]. Surface-polarity measurements using Reichardt's dye revealed that bulky tetrabutylammonium counterions substantially decrease the surface polarity of the silica support relative to NaDT, generating a more hydrophobic catalytic interface. Consequently, tetraalkylammonium decatungstate preferentially promoted the oxidation of relatively nonpolar substrates such as cyclohexane and cyclohexanol, whereas the more hydrophilic NaDT-derived surface favored the oxidation of increasingly polar alcohols, including ethanol and methanol. Electron paramagnetic resonance spin-trapping experiments further showed that these differences in surface polarity correlated with radical formation rates, providing early mechanistic evidence that

counterions can regulate substrate accessibility and reactivity by modifying the interfacial microenvironment rather than the intrinsic photochemistry of the decatungstate cluster.

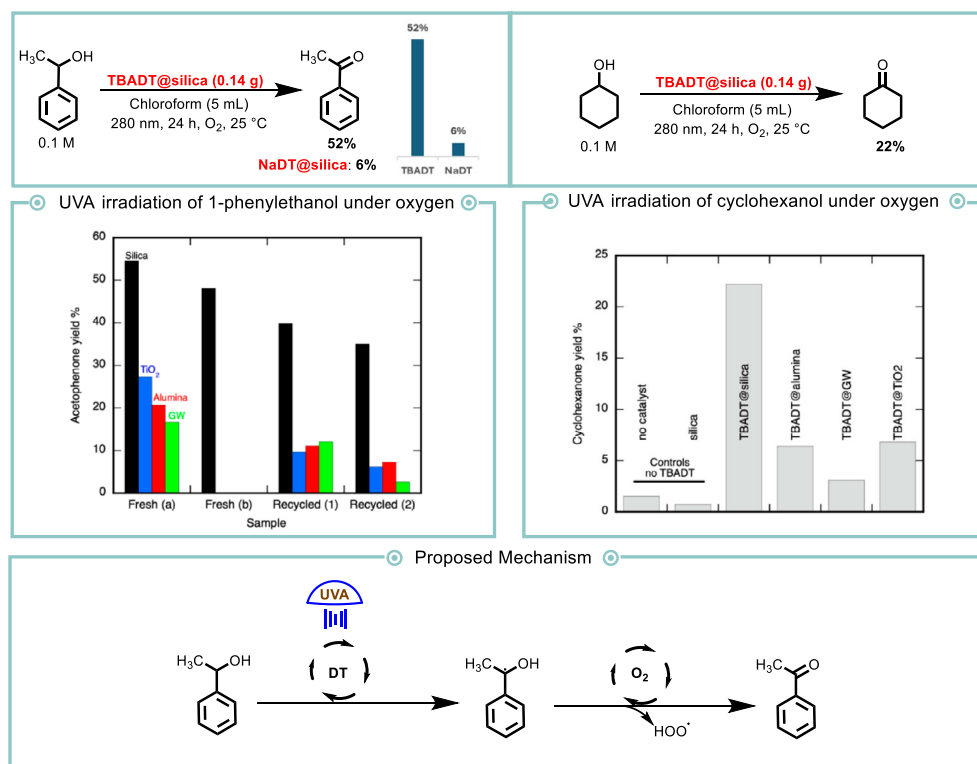
Building on these observations, Scaiano and coworkers demonstrated the immobilization of both tetrabutylammonium decatungstate (TBADT) and sodium decatungstate (NaDT) on a range of inorganic supports, including silica (SiO_2), alumina (Al_2O_3), titanium dioxide (TiO_2), and glass wool [83]. Diffuse reflectance spectroscopy confirmed that adsorption onto these materials does not significantly perturb the electronic structure of the decatungstate cluster, indicating that the fundamental ligand-to-metal charge-transfer (LMCT) photochemistry of the $[\text{W}_{10}\text{O}_{32}]^{4-}$ core is largely retained upon immobilization.

Catalytic performance, however, varies substantially with the nature of the support and the resulting interfacial environment. Under UVA irradiation, these materials were evaluated for aerobic oxidation of 1-phenylethanol to acetophenone (Scheme 15). Among the systems examined, TBADT immobilized on silica (TBADT@ SiO_2) exhibited the highest activity, affording approximately 50% yield, whereas the alumina-, TiO_2 -, and glass wool-supported analogs showed lower conversions. This enhanced performance was attributed, at least in part, to the higher surface area and pore volume of silica, as determined by Brunauer–Emmett–Teller (BET) analysis, which facilitate substrate access to the immobilized catalyst layer. Together with the favorable interfacial organization associated with the tetrabutylammonium counterion, these structural characteristics contribute to the superior catalytic performance of TBADT@ SiO_2 .

Surface functionalization introduces an additional level of control over the interfacial environment. In particular, modification of silica with 3-aminopropyltriethoxysilane (APTES), intended to improve catalyst anchoring, leads to pronounced quenching of the near-infrared phosphorescence associated with the triplet excited state of decatungstate. This observation suggests that support–catalyst interactions can influence excited-state deactivation pathways, indicating that the support functions as more than a passive scaffold and can actively modulate the local photochemical behavior of the immobilized catalyst.

A pronounced dependence on the counterion identity is also observed upon immobilization. The NaDT@silica system exhibits significantly reduced catalytic activity (approximately 6% yield), suggesting less favorable dispersion or interaction of the sodium-ion pair within the heterogeneous matrix. Notably, APTES functionalization does not substantially affect the performance of NaDT@silica, in contrast to that of TBADT-based systems. This difference is consistent with the distinct interfacial organization and ion-pairing behavior of the two catalysts under confinement.

The catalytic scope was further evaluated through the oxidation of cyclohexanol to cyclohexanone, which afforded an approximately 20% yield (Scheme 15). The lower conversion relative to the aromatic substrate is consistent with both weaker adsorption of aliphatic alcohols on the catalyst surface and the higher C–H bond dissociation energy of aliphatic systems ($92.8 \text{ kcal mol}^{-1}$) compared with that of 1-phenylethanol ($85.1 \text{ kcal mol}^{-1}$). Overall, these findings demonstrate that immobilization can



SCHEME 15 | Supported TBADT catalysts for the oxidation of 1-phenylethanol and cyclohexanol. The graphs for the UVA irradiation of 1-phenylethanol and cyclohexanol under oxygen are reproduced from ref. [83], under the Creative Commons Attribution 4.0 License (CC BY 4.0).

enable catalyst recovery and reuse while preserving the characteristic HAT reactivity of the decatungstate cluster. More importantly, they establish that counterion–surface interactions provide an additional level of control over the catalytic microenvironment, influencing substrate accessibility, interfacial organization, and ultimately catalytic performance in heterogeneous decatungstate photocatalysis.

Beyond synthetic C(sp³)–H functionalization, heterogeneous decatungstate photocatalysts have also been applied to environmental remediation, where the physicochemical properties of the support become an important determinant of the catalytic performance. Molinari and coworkers [84] demonstrated that electrostatically immobilized NaDT on aminated silica efficiently degraded cationic pharmaceuticals such as propranolol but showed little activity toward neutral carbamazepine and anionic sulfamethoxazole. This behavior was attributed to the limited ability of these substrates to access the catalyst surface, where photogenerated hydroxyl radicals were formed. In contrast, encapsulation of NaDT within a hydrophobic mesoporous organosilica matrix substantially enhanced the degradation of hydrophobic pharmaceuticals such as carbamazepine and sulfamethoxazole. The improved performance was attributed not only to the increased hydrophobicity of the support, which promotes adsorption of organic substrates, but also to the pore dimensions, which allow efficient diffusion of the pharmaceuticals into the catalyst framework and bring them into close proximity to the encapsulated decatungstate, where photogenerated hydroxyl radicals are generated. The heterogeneous catalyst also exhibited minimal decatungstate leaching and good recyclability. These findings further demonstrate that engineering the local catalytic microenvironment through support design provides an effective strategy for tuning heterogeneous decatungstate photocatalysis beyond synthetic applications.

5 | Summary and Outlook

Recent studies demonstrate that the counterion in decatungstate photocatalysis is far from a passive spectator and can significantly influence catalytic reactivity. Across sodium, ammonium, phosphonium, ionic liquid-based, and immobilized systems, counterion identity affects solubility, ion pairing, aggregation behavior, catalyst stability, electrostatic interactions, substrate accessibility, and compatibility with co-catalytic reaction networks. Decatungstate photocatalysis is therefore best viewed as an inherently ion-paired system in which the performance of the photoactive [W₁₀O₃₂]^{4−} anion depends not only on its intrinsic photochemical properties but also on its associated counterion and the surrounding reaction environment.

A key insight emerging from comparative studies is that counterion effects are strongly context-dependent rather than universally directional. In aqueous, multiphasic, or dual-catalytic systems involving redox-active co-catalysts, sodium decatungstate (NaDT) can exhibit superior performance, often attributed to its favorable stability and interfacial behavior. By contrast, tetrabutylammonium decatungstate (TBADT) is generally more effective in homogeneous organic media, where high solubility and efficient access to transient radical intermediates can favor productive reactivity. In several systems, however, the relative

performance of these salts can be reversed by changes in solvent, additives, or catalytic partners. These observations highlight that counterion effects arise from the interplay between catalyst structure, reaction environment, and mechanistic regime rather than from the intrinsic properties of the counterion alone.

Beyond these widely used systems, alternative counterion strategies have expanded the operational landscape of decatungstate photocatalysis. Phosphonium-based decatungstates can modify ion-pairing and solvation environments while also enhancing counterion stability, thereby improving catalyst durability and recyclability under prolonged irradiation while preserving the intrinsic photochemistry of the decatungstate core. Decatungstate-based ionic liquids extend this concept further by creating structured ionic media in which the catalyst itself forms an integral component of the reaction environment, enabling high catalyst loadings, enhanced phase compatibility, and simplified catalyst recovery. In parallel, immobilized systems extend decatungstate photocatalysis into heterogeneous environments, where support interactions, surface polarity, pore architecture, and interfacial organization introduce additional levels of control while enabling catalyst recovery and reuse.

Taken together, these findings suggest several general design principles for decatungstate photocatalysis:

- The counterion selection should be tailored to the reaction medium and catalytic regime. Smaller, more strongly coordinating cations such as Na⁺ can be advantageous in heterogeneous or multiphasic systems, whereas larger, weakly coordinating cations such as tetrabutylammonium or phosphonium ions can be better suited to homogeneous organic environments.
- Counterion stability under photochemical and redox conditions is critical. This consideration is particularly important in prolonged photochemical reactions and dual catalytic systems, where organic counterions may themselves undergo hydrogen-atom abstraction and subsequent decomposition.
- Solubility alone is not a reliable predictor of the catalytic performance. Ion pairing, aggregation, catalyst–substrate organization, and the local catalytic microenvironment can all influence productive catalyst–substrate encounters and, consequently, reaction outcomes.
- Electrostatic catalyst–substrate interactions provide an additional means of controlling reactivity. Attractive interactions between the anionic decatungstate catalyst and cationic substrates can influence HAT kinetics and site selectivity, complementing conventional considerations of C–H bond strength, steric accessibility, and polarity effects.
- Support engineering provides an additional strategy for controlling the catalytic microenvironment. In heterogeneous systems, surface polarity, hydrophobicity, pore architecture, catalyst–support interactions, and interfacial organization can substantially influence substrate accessibility, catalyst stability, and overall photocatalytic performance.
- Ionic-liquid-based decatungstate systems provide a versatile platform for integrating catalysis and reaction-medium design. Such systems can enable high catalyst loading,

improved phase compatibility, and simplified catalyst recovery while providing opportunities to tune the local ionic environment surrounding the photoactive species.

Despite significant progress, a detailed mechanistic picture of how counterions influence decatungstate photocatalysis remains incomplete. Future studies should seek to establish quantitative relationships between the ion-pair structure, catalyst–substrate organization, and catalytic performance across both homogeneous and heterogeneous systems. In particular, it will be important to determine how counterions interact cooperatively with solvent molecules, catalyst supports, substrates, and the excited-state dynamics of the $[W_{10}O_{32}]^{4-}$ cluster under actual catalytic conditions. Addressing these questions will require the integration of time-resolved spectroscopic methods with computational approaches capable of describing explicit solvent-, counterion-, substrate-, and interface-dependent ensembles under reaction conditions. Such efforts will be essential for establishing quantitative structure–reactivity relationships and developing predictive design principles for next-generation decatungstate photocatalysts.

Looking forward, counterion identity represents an additional structural dimension for tuning decatungstate photocatalysis, complementary to substrate design, reaction medium, and catalytic manifold. Rather than serving solely as a charge-balancing species or a solubility modifier, the counterion should be regarded as a tunable component of the catalytic microenvironment that can influence catalyst stability, substrate accessibility, reaction kinetics, site selectivity, interfacial organization, and operational robustness. Continued exploration of alternative ionic architectures, electrostatic catalyst–substrate interactions, and engineered heterogeneous interfaces should therefore further expand the scope of decatungstate-mediated HAT photocatalysis and enable more adaptable, durable, and efficient reaction platforms.

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data that support the findings of this study are available on request from the corresponding author or are publicly available in research publication. The perspective article does not use additional primary research data.

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