

Dynamics of the dimethyl sulfide exchange of (1,3-diphenylallyl)dimethylsulfonium ions

Patrick M. Jüstel  | Petra Rovó  | Herbert Mayr  | Armin R. Ofial 

Department Chemie, Ludwig-Maximilians-Universität München, Munich, Germany

Correspondence

Armin R. Ofial, Department Chemie, Ludwig-Maximilians-Universität München, Butenandtstr. 5-13, 81377 Munich, Germany.
Email: ofial@lmu.de

In admiration of Professor Barry K. Carpenter's fundamental contributions to Physical Organic Chemistry

Abstract

The dynamics of the allylic rearrangement of the (1,3-diphenylallyl) dimethylsulfonium ion in CD_2Cl_2 , which proceeds via intermediate 1,3-diphenylallyl cations, has been investigated by variable temperature ^1H NMR spectroscopy. At low temperature, the three allylic protons give rise to an AMX system, and the two diastereotopic *S*-methyl groups resonate at different frequencies. At higher temperature, an AX_2 system for the allylic protons and a single signal for the *S*-methyl groups are observed. The resulting exchange rate constant of $(364 \pm 2) \text{ s}^{-1}$ at 25°C , which corresponds to the rate of the heterolytic cleavage of the C–S bond, was used to explore the range of validity of the linear free energy relationship $\log k_{\text{het}}(25^\circ\text{C}) = s_f (N_f + E_f)$, which describes the rates of heterolytic cleavages by the electrofugality parameter E_f and the solvent-dependent nucleofuge-specific parameters N_f and s_f . The observed rate constant corroborates a previous conclusion that two different sets of N_f and s_f parameters may exist for the same nucleofuge. Knowledge of whether the reverse bond-forming reaction occurs under activation or under diffusion control is crucial for the choice of the appropriate set of nucleofugality parameters.

KEYWORDS

chalcogenides, heterolysis, kinetics, line shape analysis, linear free energy relationships

1 | INTRODUCTION

Dialkyl sulfides are strong nucleophiles, comparable with pyridine and *N*-methylimidazole.^[1] On the other hand, dialkyl sulfides are much weaker Lewis bases than these *N*-heterocycles, which makes their Lewis adducts with carbocations R^+ less stable than those generated by reactions of R^+ with *N*-heterocycles of comparable nucleophilicity.^[1,2] The combination of both properties, low intrinsic barriers and weak Lewis basicities, gives also

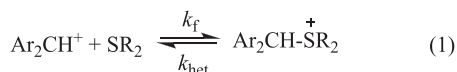
rise to the high speed of the reverse reactions, that is, the fast heterolytic scissions of sulfonium ions.^[1,3–5] In other words, dialkyl sulfides are characterized by high nucleophilicity as well as by high nucleofugality (leaving group ability),^[1] which explains their ability to act as organocatalysts.^[6–11]

Recently, we derived rate constants k_{het} for the carbon–sulfur bond cleavage of dialkyl (diarylmethyl)sulfonium ions ($\text{Ar}_2\text{CH}^+\text{SR}_2$) from the ratio k_f/K , where k_f is the second-order rate constant for the reaction of

This is an open access article under the terms of the [Creative Commons Attribution](#) License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

© 2021 The Authors. *Journal of Physical Organic Chemistry* published by John Wiley & Sons Ltd.

benzhydrylium ions with dialkyl sulfides (Equation 1) and $K (= k_f/k_{het})$ is the equilibrium constant for the corresponding reaction in dichloromethane.^[1]



It has been reported that the rates of $\text{S}_{\text{N}}1$ reactions can generally be calculated by Equation (2), where E_f represents an solvent-independent electrofugality parameter for the carbocation and the solvent-specific parameters N_f and s_f characterize the nucleofuges.^[12–14]

$$\log k_{het}(25^\circ\text{C}) = s_f(E_f + N_f) \quad (2)$$

When trying to quantify N_f and s_f of these dialkyl sulfides in the common way by plotting the rate constants of the heterolytic cleavages (k_{het} in CH_2Cl_2) of alkoxy-substituted benzhydrylsulfonium ions 1^+ against the corresponding electrofugalities of the benzhydrylium ions, we arrived at nucleofugality parameters N_f for dialkyl sulfides that were more than two orders of magnitude larger than those previously derived by Jurić, Denegri, and Kronja from solvolysis rates of unsubstituted and halogen-substituted benzhydrylsulfonium ions 2^+ .^[3–5]

We rationalized this observation by the differences of the transition states of the two reaction series (Figure 1)^[1]: The carbocationic character of the benzhydrylium ions is only partially developed in

the heterolyses of 1^+ , which give highly stabilized benzhydrylium ions (Figure 1A). In solvolysis reactions of 2^+ , which proceed via non-stabilized benzhydrylium ions, carbocationic character is fully developed in the transition state (Figure 1B; subsequent reaction with solvent not drawn).

Because this observation is of fundamental significance for the applicability of Equation (2) to predict absolute heterolysis rate constants of C–X bonds from the electrofugality parameter E_f of carbenium ions and the solvent-dependent nucleofuge-specific parameters N_f and s_f of leaving groups,^[13,14] we have now investigated the heterolysis rates of the (1,3-diphenylallyl) dimethylsulfonium ion 4^+ by dynamic NMR spectroscopy (DNMR).^[15–17]

2 | EXPERIMENTAL

2.1 | 1,3-Diphenylallyl chloride (3)

(*E*)-1,3-Diphenylprop-2-en-1-ol (0.172 g, 0.818 mmol)^[18] was dissolved in dichloromethane (3 ml) at 0°C. After adding thionyl chloride (0.136 g, 1.14 mmol, 1.4 equiv), the solution was stirred for 2 h at 0°C. Subsequently, the solvent was removed under reduced pressure. The colorless solid residue (0.186 g, 99%) was analyzed by ^1H NMR spectroscopy and used without further purification. ^1H NMR (400 MHz, CDCl_3)^[19]: δ 7.50–7.47 (m, 2 H, Ph), 7.42–7.27 (m, 8 H, Ph), 6.64 (d, $J = 15.6$ Hz, 1 H, 5-H), 6.53 (dd, $J = 15.6, 7.7$ Hz, 1 H, 6-H), 5.66 (d, $J = 7.7$ Hz, 1 H, 7-H); in accord with reported data in ref.^[20]

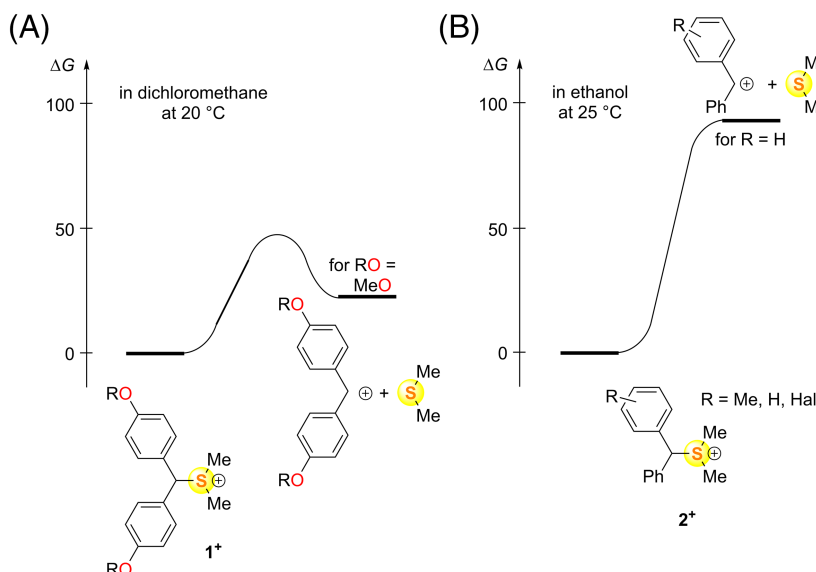


FIGURE 1 Gibbs energy profiles for heterolyses of differently substituted benzhydryldimethylsulfonium ions yielding (A) highly stabilized or (B) non-stabilized benzhydrylium ions

2.2 | Dynamic NMR spectroscopy

2.2.1 | Sample preparation

(1,3-Diphenylallyl)dimethylsulfonium triflate (4^+ TfO $^-$) was generated by dissolving the allyl chloride **3**, dimethyl sulfide (**5**, 1.5 to 4.5 equiv), and trimethylsilyl triflate (TMSOTf, 1.05 equiv) in CD₂Cl₂. The ¹H NMR spectrum (400 MHz) of the resulting solution at -70°C (Supporting Information) showed the quantitative consumption of **3** and the exclusive formation of 4^+ TfO $^-$: ¹H NMR (400 MHz, -70°C , CD₂Cl₂)^[19]: δ 7.59–7.55 (m, 2 H, Ph), 7.48–7.44 (m, 5 H, Ph), 7.35–7.31 (m, 3 H, Ph), 7.09 (d, $J = 15.5$ Hz, 1 H, 5-H), 6.43 (dd, $J = 15.4, 10.6$ Hz, 1 H, 4-H), 5.71 (d, $J = 10.5$ Hz, 1 H, 3-H), 2.95 (s, 3 H, 1-H or 2-H), 2.66 (s, 3 H, 1-H or 2-H), 2.04 (s, 6 H, free Me₂S).

2.2.2 | Temperature-dependent NMR measurements

¹H NMR spectra (400 MHz) of CD₂Cl₂ solutions of 4^+ TfO $^-$ and variable amounts of dimethyl sulfide (**5**) were

measured at variable temperature (5 K increments). Line shape analysis (LSA) of broadened resonances in the temperature range between -10 and $+20^\circ\text{C}$ was performed by manual fitting with simulated spectra generated by the DNMR6 algorithm of the *i*NMR software.^[21] The obtained rate constants were analyzed by the Eyring equation (3) to determine the activation parameters ΔH^\ddagger and ΔS^\ddagger .

$$\ln(k/T) = (-\Delta H^\ddagger/R) \times (1/T) + \ln(k_B/h) + \Delta S^\ddagger/R \quad (3)$$

The activation parameters ΔH^\ddagger and ΔS^\ddagger from Equation (3) were used to extrapolate the rate constant k (25°C).

3 | RESULTS

When 1,3-diphenylallyl chloride (**3**) was treated with trimethylsilyl triflate (1.05 equiv) and 3 equivalents of dimethyl sulfide (**5**) in CD₂Cl₂, the ¹H NMR spectra depicted in Figure 2 were obtained. At -70°C , one can assign three resonances to different S-methyl groups; two

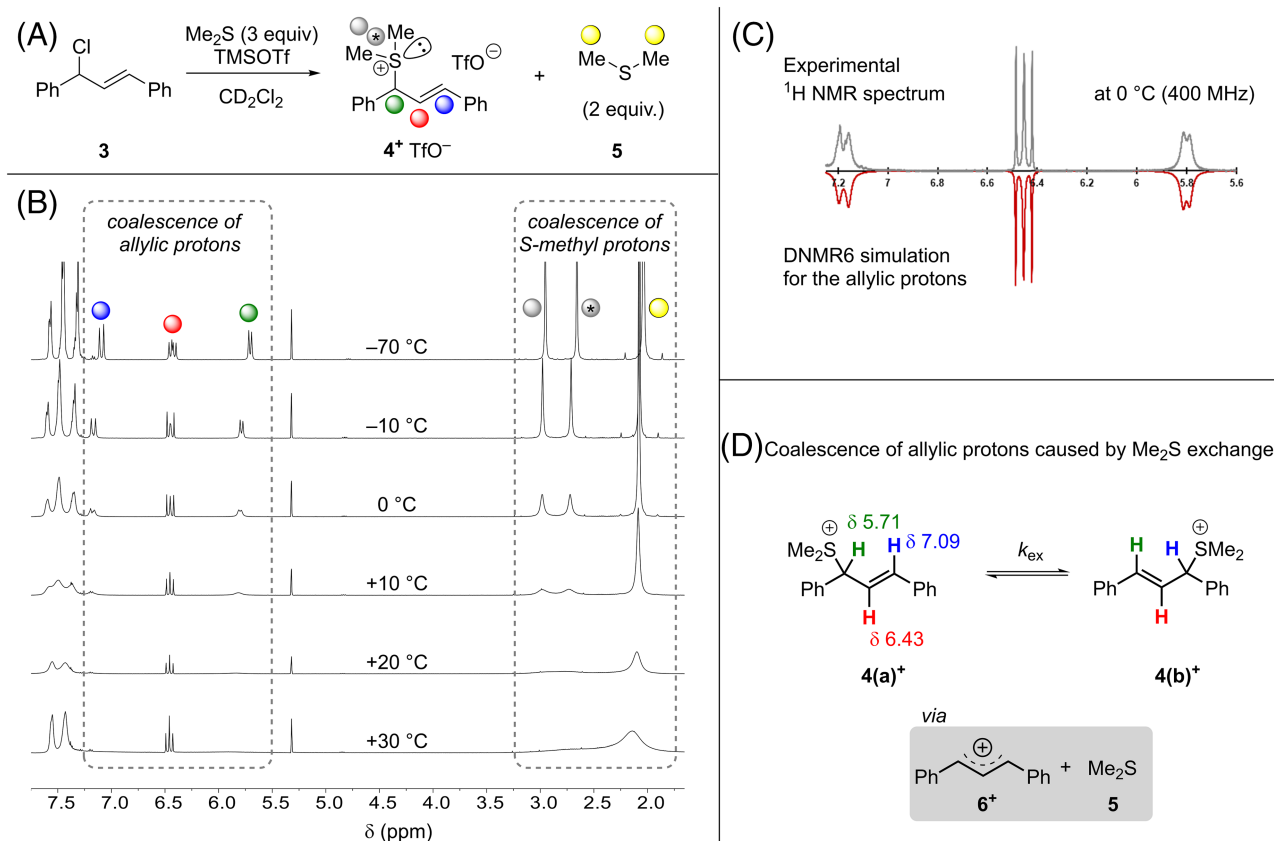


FIGURE 2 (A) Synthesis of 4^+ TfO $^-$ with excess Me₂S (**5**). (B) ¹H NMR spectra (400 MHz) of a mixture of 4^+ with Me₂S (**5**) (2 equiv) in CD₂Cl₂ at variable temperatures. Protons used for line shape analysis are marked by colored circles. (C) Experimental and simulated ¹H NMR (400 MHz) spectra at 0°C used to determine k_{ex} from resonances of allylic protons. (D) Mutual exchange reaction observed in the DNMR studies of 4^+ /**5** mixtures in CD₂Cl₂ (chemical shifts refer to -70°C)

of them are the diastereotopic *S*-methyl groups in the sulfonium ion **4**⁺ (δ 2.95 and 2.66 ppm), and one resonance is due to the unbound **5** (δ 2.04 ppm). When raising the temperature, the resonances of the diastereotopic *S*-methyl groups of **4**⁺ and that of external Me₂S (**5**) coalesce. Simultaneously, the AMX pattern of the allylic resonances (marked with green, red, and blue dots in Figure 2) converges into an AX₂ spectrum. At +20 and +30°C, only the well-resolved triplet of the central 2-CH group (red) can be seen, whereas the coalesced signal for 1-H and 3-H protons is still broadened to an extent that it cannot be spotted in Figure 2B.

Because free 1,3-diphenylallyl cations **6**⁺ were not observable in any of the experiments, one can conclude that the equilibrium is always on the side of the sulfonium ions **4**⁺. Consequently, the heterolytic cleavage of the sulfonium ion **4**⁺ must be slower than the recombination of allyl cation **6**⁺ with Me₂S (**5**). Accordingly, the rate of the exchange of the SCH₃ signals as well as that of the allylic protons must be controlled by the heterolysis of **4**⁺. The broadening of the resonances for the diastereotopic *S*-methyl groups in **4**⁺ is coupled with the exchange with Me₂S from the solution, however, and cannot be analyzed straightforwardly. We have, therefore, considered the allylic region of the temperature-dependent ¹H NMR spectra to derive information on the rate of the C–S bond-breaking reaction.

Hence, allylic proton signals of **4**⁺ at δ 7.09, 6.43, and 5.71 ppm were analyzed by LSA (Figure 2C) in the temperature range between –10 and +20°C (5 K increments; only a selection of spectra is shown in Figure 2B). Line broadening of the allylic protons is caused by mutual exchange between **4(a)**⁺ and **4(b)**⁺ (Figure 2D). The frequency of this exchange reaction between sulfonium ions **4**⁺ is described by the temperature-dependent exchange rate constant k_{ex} (s^{–1}).

Analogous DNMR studies of solutions with 3.5, 2.0, or 0.5 equivalents of non-bound Me₂S (**5**) gave almost

identical k_{ex} values at each of the investigated temperatures (Table 1). Given that the Me₂S concentration does not influence the rate of the exchange process, the occurrence of S_N2 (or S_N2') mechanisms can be excluded. From the Eyring activation parameters [$\Delta H^\ddagger = (69.4 \pm 0.2)$ kJ mol^{–1}, $\Delta S^\ddagger = (37.0 \pm 0.7)$ J mol^{–1} K^{–1}] for the combined $k_{\text{ex}}(T)$ data of the three independent series of measurements at different Me₂S concentrations, an exchange rate constant $k_{\text{ex}}(25^\circ\text{C}) = (364 \pm 2)$ s^{–1} was determined. On a molecular level, we assign k_{ex} to the rate constant k_{het} for the heterolytic C–S bond cleavage in **4**⁺ to give Me₂S (**5**) and the allyl cation **6**⁺ as depicted in Figure 2D.

We could not analyze in detail the exchange processes that caused the coalescence phenomena for the *S*-methyl groups. Nevertheless, the broadening of the resonance for the excess Me₂S (**5**) occurs in the same temperature range as the evaluated allyl isomerization, which indicates comparable exchange rates and a significant participation of free Me₂S (**5**) in the dynamics. We, therefore, exclude that intramolecular 1,3-migrations of the Me₂S group in **4**⁺ contribute significantly to the observed exchange reaction.

4 | DISCUSSION

Recently, it was found that heterolysis rate constants for the benzhydryldimethylsulfonium ions **1**⁺ and **2**⁺, in which the electrofugalities of the benzhydryl moieties are varied over a wide range, cannot be described by a single set of nucleofugality parameters N_f and s_f for the Me₂S nucleofuge.^[1]

In general, N_f and s_f parameters in Equation (2) describe the leaving group ability of a certain nucleofuge in a certain solvent.^[12,14] It has long been known that the leaving group abilities of anionic nucleofuges (e.g., chloride, bromide, and tosylate anions) vary over several orders of magnitude in protic solvents of variable

<i>T</i> (°C)	k_{ex} (s ^{–1})		
	4 ⁺ + 5 (0.5 equiv) ^a	4 ⁺ + 5 (2.0 equiv) ^b	4 ⁺ + 5 (3.5 equiv) ^c
–10	7.7	7.7	7.7
–5	14.3	14.3	14.3
0	26.0	26.0	26.0
+5	46.0	46.0	46.0
+10	76.0	78.0	76.0
+15	132	132	132
+20	225	225	225

TABLE 1 Temperature-dependent DNMR exchange rate constants $k_{\text{ex}}(T)$ for mixtures of **4**⁺ and Me₂S (**5**) in CD₂Cl₂

^aGenerated by mixing **3** (0.077 mmol), TMSOTf (1 equiv), and Me₂S (**5**, 1.5 equiv) in CD₂Cl₂ (0.7 mL).

^bGenerated by mixing **3** (0.077 mmol), TMSOTf (1 equiv), and Me₂S (**5**, 3.0 equiv) in CD₂Cl₂ (0.7 mL).

^cGenerated by mixing **3** (0.077 mmol), TMSOTf (1 equiv), and Me₂S (**5**, 4.5 equiv) in CD₂Cl₂ (0.7 mL).

composition. Generally, the solvent dependence decreases with decreasing need for anion solvation.^[12] Benzhydryldimethylsulfonium ions generate the neutral leaving group Me₂S, and the corresponding solvolysis rate constants have been studied in detail by Kevill and coworkers in 35 solvents.^[22] When reactions in the slightly acidic solvent mixtures of fluorinated alcohols (i.e., aq TFE or aq HFIP mixtures) are disregarded, solvolysis rate constants for the [Ph₂CH-SMe₂]⁺ ion fluctuated by about one order of magnitude when the solvents were varied from 95/5 dioxane/water mixtures ($k_{\text{solv}} = 0.75 \times 10^{-4} \text{ s}^{-1}$) to pure methanol ($k_{\text{solv}} = 7.88 \times 10^{-4} \text{ s}^{-1}$). Destabilization of the reactant ground state of [Ar₂CH-SMe₂]⁺ in less polar solvents has been suggested to rationalize why the nucleofugality of Me₂S tends to increase mildly with decreasing solvent polarity in aqueous alcohol mixtures.^[3,23]

Figure 3 illustrates the separation of the two data sets reported in ref.^[11]: Based on previously reported solvent effects on the carbon–sulfur bond cleavage rates of benzhydryldimethylsulfonium ions,^[3,22] it is not surprising that extrapolation of the ethanolysis rate constants of the benzhydryldimethylsulfonium ions **2a**⁺–**2e**⁺ on the left does not perfectly merge with the correlation line for the heterolysis rates of the benzhydryldimethylsulfonium ions **1a**⁺–**1c**⁺ in dichloromethane on the right. Because the nucleofugalities of neutral leaving groups are only marginally affected by the solvent,^[3–5,14,22–24] however, the large separation by almost a factor of thousand could not be due to the fact that the heterolyses of the

sulfonium ions **2a**⁺–**2e**⁺ were investigated in ethanol but the heterolysis reactions of **1a**⁺–**1c**⁺ refer to dichloromethane solution. Rather, this difference was explained by the fact that the solvolysis reactions of sulfonium ions derived from non-stabilized benzhydrylium ions on the left (i.e., **2a**⁺–**2e**⁺) proceed via transition states, which equal the separated products, benzhydrylium ions **8a**⁺–**8e**⁺ and Me₂S (cf. Figure 1B), whereas in the heterolyses of sulfonium ions derived from alkoxy-substituted benzhydrylium ions **7a**⁺–**7c**⁺ on the right (i.e., **1a**⁺–**1c**⁺), the benzhydrylium ion character is not yet fully developed in the transition state (cf. Figure 1A). Why does the heterolysis rate constant of **4**⁺ (with formation of **6**⁺, $E_f = -0.46$ ^[25]) better match the correlation line defined by the sulfonium ions **2a**⁺–**2e**⁺ (deviation by a factor of 7.6) than that of the alkoxy-substituted analogues **1a**⁺–**1c**⁺ with similar electrofugalities (deviation by a factor of 1/55)?

One reason might be that Equation (2), which was derived from solvolysis rates of benzhydryl-model compounds, is less reliable when applied to solvolysis reactions that generate structurally different types of carbocations. It has been shown, however, that electrofugality parameters E_f for aryl-substituted carbocations that were calculated from individual solvolysis reactions with different leaving groups in different solvents scatter only slightly around the optimum E_f value (± 0.4 at maximum; for the 1-phenylallylium ion: ± 0.24).^[13] The optimized E_f parameter for carbenium ion **6**⁺ was obtained from a series of solvolysis kinetics that comprised three

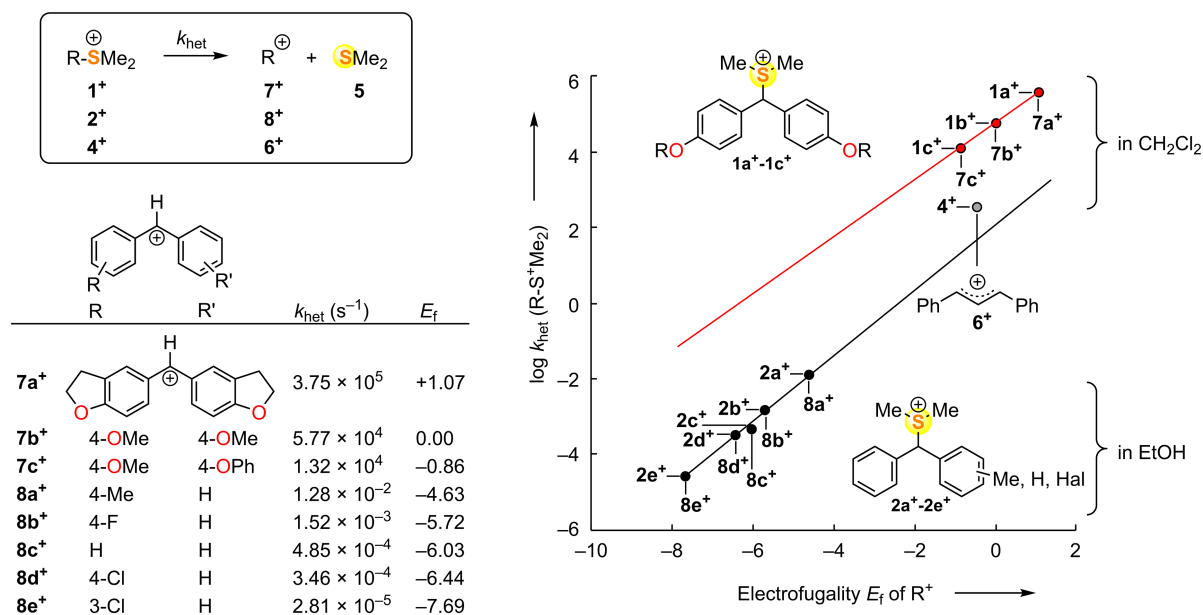


FIGURE 3 Correlation of the heterolysis rate constants of benzhydryldimethylsulfonium ions **1**⁺ and **2**⁺ and the (1,3-diphenylallyl) dimethylsulfonium ion **4**⁺ with the electrofugality parameters E_f of the resulting carbenium ions **6**⁺, **7**⁺, and **8**⁺ (k_{het} at 20 or 25°C from refs.^[1,3]; E_f from refs.^[14,25])

different leaving groups and seven solvent mixtures and covered an overall reactivity range of more than six orders of magnitude. Nevertheless, none of the individual rate constants deviated more than by a factor of 3.2 from the solvolysis rate constants calculated by Equation (2) and the optimized $E_f = -0.46$.^[25]

Notably, the electrophilicity of allyl cation 6^+ ($E = 2.70$)^[26] is almost 3 orders of magnitude greater than that of $7b^+$ ($E = 0.0$) though the electrofugalities E_f of these two carbenium ions are very similar (abscissa of Figure 3). From the electrophilicity $E = 2.70$ for 6^+ and the recently published nucleophilicity parameters $N = 12.32$, $s_N = 0.72$ for Me_2S (5) in dichloromethane,^[1] one can calculate (by Equation 4) a second-order rate constant of $k_2 = 6.5 \times 10^{10} M^{-1} s^{-1}$ for the reaction of 6^+ with Me_2S , that is, this bond-forming reaction is diffusion-controlled.

$$\log k_2(20^\circ C) = s_N(N + E) \quad (4)$$

Application of the principle of microscopic reversibility leads to the conclusion that the heterolysis of the allylsulfonium ion 4^+ proceeds through a transition state that corresponds to the products like the benzhydryl-substituted sulfonium ions 2^+ illustrated in Figure 1B, but unlike the sulfonium ions 1^+ depicted in Figure 1A. For that reason, the heterolysis rate of the allylsulfonium ion 4^+ is better described by the nucleofugality parameters N_f/s_f for Me_2S (5) derived from the solvolysis rates of 2^+ , which form non-stabilized benzhydrylium ions 8^+ ,^[3–5,24] than by those determined from the solvolysis rates of 1^+ , which give stabilized alkoxy-substituted benzhydrylium ions 7^+ .^[1]

5 | CONCLUSIONS

Investigations of the kinetics of numerous bond-forming reactions of carbenium ions with nucleophiles have shown that Equation (4) is well suited for predicting second-order rate constants k_2 (at 20°C), if k_2 is smaller than $10^8 M^{-1} s^{-1}$.^[27] Equation (4) does not hold for faster reactions, however, where the diffusion rates become dominant.^[27,28] Because S_N1 reactions must proceed through the same transition states as the reverse reactions (principle of microscopic reversibility), we had previously reported that the linear correlations between the rate constants of S_N1 reactions and Lewis acidities of the resulting carbenium ions break down when the reverse reactions (reactions of carbocations with the leaving groups) change from diffusion to activation control.^[27,29] Only recently we have observed that the switchover from activation to diffusion control of the

reverse (bond-forming) reactions also limits the range of validity of Equation (2).^[1]

The heterolysis rate constant of the allylsulfonium ion 4^+ reported in this work is in line with this interpretation and underlines the role of the rate of the reverse reaction, that is, recombination of the carbocation with the leaving group, for defining the applicability of Equation (2) to describe the heterolytic scission of C–X σ -bonds.

Whereas the limitation of Equation (4), which describes the rate constants of the electrophile nucleophile combinations, can easily be recognized by the fact that calculated rate constants $>10^{10} M^{-1} s^{-1}$ cannot exist because of the diffusion limit (k approx. $10^{10} M^{-1} s^{-1}$), the situation is more complex for Equation (2), because its application requires consideration of the reverse reaction.

ACKNOWLEDGEMENTS

We thank Dr. David Stephenson and Claudia Ober for help with the NMR experiments.

DATA AVAILABILITY STATEMENT

Data available on request from the authors.

ORCID

Patrick M. Jüstel  <https://orcid.org/0000-0002-1857-5916>

Petra Rovó  <https://orcid.org/0000-0001-8729-7326>

Herbert Mayr  <https://orcid.org/0000-0003-0768-5199>

Armin R. Ofial  <https://orcid.org/0000-0002-9600-2793>

REFERENCES

- [1] B. Maji, X.-H. Duan, P. M. Jüstel, P. A. Byrne, A. R. Ofial, H. Mayr, *Chem. – Eur. J.* **2021**. EarlyView. <https://doi.org/10.1002/chem.202100977>
- [2] H. Mayr, J. Ammer, M. Baidya, B. Maji, T. A. Nigst, A. R. Ofial, T. Singer, *J. Am. Chem. Soc.* **2015**, *137*, 2580.
- [3] S. Jurić, B. Denegri, O. Kronja, *J. Org. Chem.* **2010**, *75*, 3851.
- [4] S. Jurić, B. Denegri, O. Kronja, *J. Phys. Org. Chem.* **2012**, *25*, 147.
- [5] B. Denegri, M. Matic, O. Kronja, *Synthesis* **2017**, *49*, 3422.
- [6] R. Okazaki, N. Tokitoh, V. K. Aggarwal, C. L. Winn, *Encyclopedia of Reagents for Organic Synthesis*, Wiley, New York **2006**. <https://doi.org/10.1002/047084289X.rd372.pub2>
- [7] A.-H. Li, L.-X. Dai, V. K. Aggarwal, *Chem. Rev.* **1997**, *97*, 2341.
- [8] E. M. McGarrigle, E. L. Myers, O. Illa, M. A. Shaw, S. L. Riches, V. K. Aggarwal, *Chem. Rev.* **2007**, *107*, 5841.
- [9] D. Basavaiah, A. J. Rao, T. Satyanarayana, *Chem. Rev.* **2003**, *103*, 811.
- [10] D. Basavaiah, B. S. Reddy, S. S. Badsara, *Chem. Rev.* **2010**, *110*, 5447.
- [11] D. Basavaiah, R. T. Naganaboina, *New J. Chem.* **2018**, *42*, 14036.
- [12] a) B. Denegri, A. Streiter, S. Jurić, A. R. Ofial, O. Kronja, H. Mayr, *Chem. – Eur. J.* **2006**, *12*, 1648; b) B. Denegri, A. Streiter,

- S. Jurić, A. R. Ofial, O. Kronja, H. Mayr, *Chem. – Eur. J.* **2006**, *12*, 5415.
- [13] B. Denegri, A. R. Ofial, S. Jurić, A. Streiter, O. Kronja, H. Mayr, *Chem. – Eur. J.* **2006**, *12*, 1657.
- [14] N. Streidl, B. Denegri, O. Kronja, H. Mayr, *Acc. Chem. Res.* **2010**, *43*, 1537.
- [15] D. Darwish, G. Tourigny, *J. Am. Chem. Soc.* **1966**, *88*, 4303.
- [16] M. Nakamura, H. Kihara, N. Nakamura, M. Oki, *Org. Magn. Reson.* **1979**, *12*, 702.
- [17] D. Darwish, S. H. Hui, R. Tomilson, *J. Am. Chem. Soc.* **1968**, *90*, 5631.
- [18] J. M. Dickinson, J. A. Murphy, C. W. Patterson, N. F. Wooster, *J. Chem. Soc. Perkin Trans. 1* **1980**, 1179.
- [19] See the Supporting Information for atom labelling.
- [20] M. A. Tandiry, Y. Masui, M. Onaka, *Synlett* **2014**, *25*, 2639.
- [21] Mestrelab Research, iNMR for Windows (version 6.1.8), <http://www.inmr.net>, **2018**.
- [22] D. N. Kevill, S. W. Anderson, N. H. Ismail, *J. Org. Chem.* **1996**, *61*, 7256.
- [23] M. Matic, B. Denegri, S. Jurić, O. Kronja, *Croat. Chem. Acta* **2017**, *90*, 571.
- [24] S. Jurić, B. Portolan, O. Kronja, *Croat. Chem. Acta* **2016**, *89*, 65.
- [25] K. Troshin, H. Mayr, *J. Org. Chem.* **2013**, *78*, 2649.
- [26] K. Troshin, C. Schindele, H. Mayr, *J. Org. Chem.* **2011**, *76*, 9391.
- [27] H. Mayr, A. R. Ofial, *Acc. Chem. Res.* **2016**, *49*, 952.
- [28] J. Ammer, C. Nolte, H. Mayr, *J. Am. Chem. Soc.* **2012**, *134*, 13902.
- [29] H. Mayr, A. R. Ofial, *Pure Appl. Chem.* **2017**, *89*, 729.

SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.

How to cite this article: P. M. Jüstel, P. Rovó, H. Mayr, A. R. Ofial, *J Phys Org Chem* **2022**, *35*(11), e4270. <https://doi.org/10.1002/poc.4270>