all concentrations of benzene and DBA studied, the fluorescence decay curves could be described by the sum of two exponentials only. In contrast, a third exponential with a *negative* coefficient is *always* present in the quenching of ${}^3A^*$ by Xy (0.8–8.3 M). Thus in this case, dissociation of the exciplex is slow compared to its other modes of deactivation.

As expected, in neat cyclohexane (no Xy), the decay of DBA fluorescence sensitized by ${}^3A^*$ shows no second maximum. The subsequent slow exponential decay ($k_{obs} = k_d{}^A + k_{ET}{}^A[DBA]$) indicates that $k_d{}^A = 1.7 \times 10^6$ s^{-1} (compared to 2.0×10^6 s^{-1} in the case of acetone).

The buildup to a second maximum in the presence of Xy (even at 0.8 M, the lowest Xy concentration studied) requires (a) that ${}^3A^*$ and ${}^3E^*$ decay at different rates and (b) that ${}^3E^*$ be a sensitizer of DBA fluorescence. In fact, the S_1 state of DBA is populated *more efficiently* from ${}^3E^*$ than from ${}^3A^*$ (i.e., $\phi_{TS}{}^E > \phi_{TS}{}^A$, in Scheme I), as in the case of the acetone/benzene system.[2] This is shown in Figure 2, where $\phi_{TS}{}^{exp}$, the fraction of ${}^3A^*$ molecules which produce ${}^1DBA^*$ either directly or via an exciplex, is given by[5]

$$\phi_{TS}{}^{exp} = \left(\frac{N_s}{N_p}\right)\frac{\epsilon_{DBA}[DBA]}{\epsilon_A[A]}$$

N_p and N_s (in counts) are the integrated intensities of the prompt (the result of direct excitation of DBA) and slow emission (sensitized by ${}^3A^*$), respectively. $\epsilon_{DBA}[DBA]/\epsilon_A[A]$ is the ratio of the partial absorbances of DBA and A in the mixed solution. At [DBA] = 5×10^{-4} M (Figure 2), $\phi_{TS}{}^{exp}$ is ~3 times higher in *o*-xylene than in cyclohexane. Interestingly, this higher energy transfer efficiency is an intrinsic property of the exciplex, rather than a kinetic property of the system, since the lifetime of the exciplex is *shorter* than that of the uncomplexed triplet ketone in the same solution (i.e., ~*60* ns compared to ~200 ns, under the conditions of Figure 1). At a given concentration of Xy, the rate of decay of ${}^3A^*$ takes the form

$$k_{obs} = k + k_{ET}{}^A[DBA]$$

with $k = k_d{}^A + k_{EA}[Xy]$.[6] We have determined that $k_{EA} \lesssim 10^6$ M^{-1} s^{-1}; thus the formation of ${}^3E^*$ is a slow process.

The contrast between the kinetics of the quenching of ${}^3A^*$ by Xy and that of triplet acetone by benzene illustrates the merits of using DBA as a tool for the characterization of nonemitting exciplexes. Interestingly, there is *no* evidence for a *long-lived* exciplex (i.e., no second peak) when ${}^3A^*$ is quenched by benzene instead of xylene. In fact, benzene is a less efficient "quencher" of ${}^3A^*$ than is *o*-xylene (smaller k_{obs} at the same DBA and quencher concentrations). The fluorescence decay curves are simple double-exponential functions, and $\phi_{TS}{}^{exp}$ appears to be no greater than it is in neat cyclohexane.

The order of quenching efficiency is reversed in the case of triplet acetone, which is more effectively quenched by benzene than by *o*-xylene. No second maximum is observed with either quencher nor in the quenching of 2-hexanone by *o*-xylene (3.2 M, as in the experiment of Figure 1), all at 20 °C. On the other hand, 3-pentanone and DBA in mixed cyclohexane/*o*-xylene produced a fluorescence intensity profile very similar to that of Figure 1, thus clearly indicative of a relatively stable exciplex.

The rate of formation and the stability of such triplet exciplexes seem therefore to be quite subtly dependent on the electronic and structural properties of both the aromatic quencher and alkanone quenchee. DBA, with its ability to scavenge triplet excitation energy and reemit it (with a ~2-ns lifetime) will help us assess the factors involved, in cases where the overall TS energy transfer is exergonic.

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(5) If exciplex dissociation is indeed unimportant, Scheme I leads to the following expression for [DBA]-dependent $\phi_{TS}{}^{exp}$ as a kinetic average of $\phi_{TS}{}^A$ and $\phi_{TS}{}^E$:

$$\phi_{TS}{}^{exp} = \phi_{EA}\phi_{ET}{}^E\phi_{TS}{}^E + \phi_{ET}{}^A\phi_{TS}{}^A$$

where $\phi_{ET}{}^E$ $\phi_{ET}{}^A$ are the efficiencies of scavenging ${}^3A^*$ and ${}^3E^*$ by DBA and ϕ_{EA} is the efficiency of exciplex formation over all other modes of deactivation of ${}^3A^*$.

(6) Experimentally, plots of k vs. [Xy] are not linear but curve upwards. This curvature may reflect the inadequacy of the kinetic treatment based on Scheme I, at the high Xy concentrations used here, where Xy is becoming the solvent. Also, a three-component exciplex AXy_2 may possibly play a role.

Carbenic Philicity: 6,6-Dimethylfulvene as an Indicator Substrate

Robert A. Moss,* Claire M. Young,† Leon A. Perez, and Karsten Krogh-Jespersen*

Wright and Rieman Laboratories, Deparment of Chemistry
Rutgers, The State University of New Jersey
New Brunswick, New Jersey 08903

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Singlet carbenes have been characterized as electrophilic,[1] ambiphilic,[2] or nucleophilic[3] on the basis of their selectivities[4] toward electron-rich and electron-poor alkenes. The variation of carbenic "philicity" with carbenic structure (i.e., X and Y in CXY) has been experimentally probed by linear free-energy analysis of carbenic relative reactivities with various series of olefinic substrates[1,4,5] and theoretically treated by molecular orbital techniques.[6-8] In previous experimental philicity determinations, subject carbenes were each studied with at least 4 or 5 olefinic substrates of varying π-electronic properties.[1,4] Consequently, one seeks a single "indicator" alkene which, by itself, could furnish an initial classification of carbenic philicity upon reaction with a given carbene.

In this vein is the observation that the regiochemistry of cyclopropanation of 1,1-dimethylallene by various ring-substituted phenylcarbenes rationally parallels the electronic properties of the phenyl substituents.[9] However, 1,1-dimethylallene is unable to differentiate ambiphilic from electrophilic carbenes[10] and is unlikely to react at all with strongly nucleophilic carbenes. A more promising candidate is 6,6-dimethylfulvene (**1**),[14] which reacts with nucleophilic lithium dichloromethide (THF, −75 °C) exclusively at its exocyclic double bond but reacts with electrophilic chlorocarbenoid (CH_2Cl_2, CH_3Li, Et_2O, −20 °C) only at an in-

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† Special Graduate School Fellow, Rutgers University.

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(10) CH_3OCCl, a bona fide ambiphile,[2] adds exclusively to the most substituted double bond of 1,1-dimethylallene,[11] as do the archetypal electrophiles CCl_2[12] and CBr_2.[12,13]

(11) Thermal decomposition (25 °C) of methoxychlorodiazirine in 1,1-dimethylallene gave 23% of 1-chloro-1-methoxy-2,2-dimethyl-3-methylenecyclopropane [bp 52 °C (25 mmHg)]. The structure was established by mass spectroscopy (*m/e*, 146, 148, M^+) and a definitive proton NMR spectrum, $\delta_{CCl_4}{}^{Me_4Si}$ 1.23, 1.35 (2 s, 6 H, CH_3's), 3.52 (s, 3 H, CH_3O), 5.43, 5.77 (2 s, 2 H, $=CH_2$). No trace of the isomeric adduct resulting from CH_3OCCl addition at $C{=}CH_2$ was observed in the NMR spectrum of the crude reaction product.

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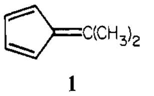
ternal double bond, affording α-methylstyrene after rearrangement and loss of HCl.[15] In this communication we show that 6,6-dimethylfulvene readily differentiates typical electrophilic from nucleophilic carbenes on the basis of their regiochemical selectivity. Moreover, we present a brief theoretical analysis of these reactions which clarifies the origins of the observed selectivities.

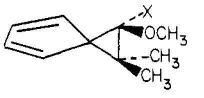
Electrophilic Carbenes. Literature examples clearly point to endocyclic attack of electrophilic carbenes on fulvenes in general and **1** in particular. Electrophilic[1] CCl_2 attacks **1**,[16a] and other



1

$(CH_3)_2C{=}C{:}$

2



3, X = Cl
4, X = OCH_3

6,6-disubstituted fulvenes,[16] exclusively at the endocyclic π bonds, generally affording *m*-chlorostyrene derivatives after rearrangement.[16] Similarly, endocyclic cyclopropanation occurs with electrophilic[17] dimethylmethylenecarbene (**2**)[18] and electrophilic[19] chlorocarbenoid.[15] In our hands, reaction of excess CCl_2 (0 °C, $CHCl_3$, 50% aqueous NaOH, catalytic $Et_3N^+CH_2C_6H_5,Cl^-$)[20] with **1** afforded 27% of *m*-chloro-α-methylstyrene and 12% of *m*-chlorocumyl chloride (based on unrecovered **1**). Both products must have arisen by initial CCl_2 attack on an endocyclic π bond of **1**. There was no evidence for formation of the regiochemically isomeric adduct, 1,1-dichloro-2,2-dimethylspiro[2.4]heptadiene. These results agree with Hart's finding of ~25% of *m*-chloro-α-methylstyrene formed from **1** and CCl_2 ($NaOOCCCl_3$, refluxing diglyme, 2–6 h).[16a]

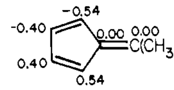
Nucleophilic Carbenes. Thermal decomposition (25 °C, 24 h) of methoxychlorodiazirine[2,21] in **1** afforded 35% of spiro[2.4]heptadiene derivative **3**, which was purified by distillation [bp 37–38 °C (18 μm)] and characterized by mass (M^+ at m/e 184, 186), ^{13}C, and ^1H NMR spectra.[22] NMR analysis of the crude reaction product and its various distillation fractions gave no evidence for regiochemically isomeric adducts of **1** and CH_3OCCl or their likely rearrangement–elimination product (i.e., *m*-methoxy-α-methylstyrene).

Pyrolysis (125 °C, 2 h) of 1,2,3,4-tetrachloro-5-phenyl-7,7-dimethoxybicyclo[2.2.1]hepta-2,5-diene[3] in nitrogen-purged, neat **1** gave spiro[2.4]heptadiene **4**, which was isolated in 8% yield by distillation [conditions, 95 °C (100 μm)], purified by GC (10% SE-30, 110 °C), and characterized by elemental analysis and ^1H NMR spectroscopy.[23] Present in the NMR spectrum of the crude reaction product were absorptions due to **1**, polymerized **1**, unreacted carbene progenitor, and side products from the latter's decomposition.[3] Despite the low yield of **4**, however, *there were no NMR signals which could reasonably be attributed to an endocyclic adduct of* $(CH_3O)_2C$ *and* **1** *or a rearrangement product of such an adduct* (e.g., *m*-methoxy-α-methylstyrene or *m*-methoxy-α-methoxycumene). Thus, both CH_3OCCl and $(CH_3O)_2C$ express strong regioselectivity for the exocyclic π bond of **1**, in contrast to such electrophilic carbenes as CCl_2 and **2** (see above).

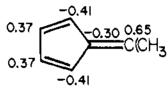
Rationale. Frontier molecular orbital (FMO) theory has been successfully used to understand the selectivities of acyclic, heteroatom-substituted carbenes toward various alkenes.[2,4,6] We now find that its application to the reactions of **1** with CCl_2, CH_3OCCl, and $(CH_3O)_2C$ provides a satisfactory rationale for the observed regioselectivities. From calculated[6] 4-31G energies (eV) of CXY LUMO's (CCl_2, 0.31; CH_3OCCl, 2.46; $(CH_3O)_2C$, 4.09) and HOMO's (−11.44, −10.82, −10.81, respectively) and using an experimental value for the HOMO of **1** (−8.08 eV)[24] and an estimated value of −0.2 eV for its LUMO,[25a] we derive the differential energies $(E_{\mathrm{CXY}}{}^{\mathrm{LU}} - E_1{}^{\mathrm{HO}})$ and $(E_1{}^{\mathrm{LU}} - E_{\mathrm{CXY}}{}^{\mathrm{HO}})$.[25b] For reaction of CCl_2 with **1**, the former difference (8.4 eV) is significantly smaller than the latter (11.2 eV), indicating dominant CCl_2-LUMO/dimethylfulvene-HOMO interaction and electrophilic addition. The reverse situation, however, is found for reaction of $(CH_3O)_2C$ and **1**, with $(E_1{}^{\mathrm{LU}} - E_{\mathrm{CXY}}{}^{\mathrm{HO}} = 10.6\ \mathrm{eV})$ the energetically smaller and dominant orbital interaction.[26] This indicates a controlling $(CH_3O)_2C$-HOMO/dimethylfulvene-LUMO interaction and hence nucleophilic addition.

Ambiphilic[2] CH_3OCCl reacts with **1** with the same regiochemistry as nucleophilic $(CH_3O)_2C$; the sense of addition is not controlled by the differential energies of the FMO interactions for these are now nearly identical (10.5, 10.6 eV). We therefore recall that the dominant FMO interaction is determined both by differential orbital energies *and overlap*.[6] In the absence of a strongly dominant energy factor, we can deduce the preferred orbital interaction on the basis of overlap.

Explicit compositions of the frontier orbitals of **1** are given by the 2p(π) coefficients obtained from an ab initio calculation on 6,6-dimethylfulvene[27a] by using the STO-3G basis set;[27b] cf. **5** (HOMO) and **6** (LUMO). Reference to **5** shows that the



5



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electrophilic attack of CCl_2 must occur at an endocyclic π bond of **1**, because the requisite fulvene HOMO has zero coefficients at the exocyclic π bond. Considering only the signs of the coefficients of the fulvene LUMO (**6**), nucleophilic attack of $(CH_3O)_2C$ is symmetry allowed at either endocyclic or exocyclic π bonds. However, the very large coefficient at C_6 makes possible substantial overlap at this site, leading to exocyclic nucleophilic addition.[28]

Finally, the apparent nucleophilicity of ambiphilic[2] CH_3OCCl, for which the alternative differential HOMO/LUMO energies in addition to **1** are nearly identical, seems to be decided by the largest possible overlap during addition. This appears to arise through the nucleophilic interaction with $C_1{=}C_6$ rather than through combined electrophilic *and* nucleophilic interaction with $C_2{=}C_3$.[29]

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(22) $\delta_{\mathrm{CCl_4}}{}^{\mathrm{Me_4Si}}$ 1.50, 1.60 (2 s, 6 H, CH_3's), 3.47 (s, 3 H, OCH_3), 6.06–6.57 (m, 4 H, vinyl). Adduct **3** was unstable to various GC and HPLC conditions and could not be obtained in >95% purity. Traces of $CH_3OClC{=}CClOCH_3$ and $CH_3OCCl{=}N\text{-}N{=}CClOCH_3$ were present (NMR)[2] in the distilled material.

(23) $\delta_{\mathrm{CCl_4}}{}^{\mathrm{Me_4Si}}$ 1.45 (s, 6 H, CH_3's), 3.32 (s, 6 H, OCH_3's), 6.10–6.50 (m, 4 H, vinyl).

(24) Taken as the negative of the vertical ionization potential: Brogli, F.; Clark, P. A.; Heilbronner, E.; Neuenschwander, M. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 422. Reference 25 gives this value as 8.03 eV.

(25) (a) Houk, K. N.; George, J. K.; Duke, R. G., Jr. *Tetrahedron* **1974**, *30*, 523. Using different methods, these authors estimated three values for the electron affinity of **1**: 0.8, 0.2, and −0.5 eV. We use the middle value, which was successfully applied in a FMO study of fulvene cycloaddition reactions. Unpublished experimental and calculational data suggest that 0.2 must be very close to the correct value (private communication from Professor K. D. Jordan, University of Pittsburgh). Our conclusions (see below) are not qualitatively affected by the specific choice among Houk's three estimates. (b) Experimental IP and EA values are not available for the carbenes of interest, but they would undoubtedly differ from the calculated orbital energies. However, as demonstrated in ref 6, the present blend of experimental and theoretical energies does lead to qualitatively useful rationalization of much experimental data. For example, there is a linear correlation of calculated carbene LUMO energies and experimental carbenic selectivities.[6]

(26) $(E_{\mathrm{CXY}}{}^{\mathrm{LU}} - E_1{}^{\mathrm{HO}}) = 12.2$ eV for $(CH_3O)_2C$ and **1**.

(27) (a) We use the experimental geometry determined by electron diffraction: Chiang, J. F.; Bauer, S. H. *J. Am. Chem. Soc.* **1970**, *92*, 261. (b) Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657. The calculations employed the GAUSSIAN 70 series of programs: Hehre, W. J.; Lathan, W. A.; Ditchfield, R.; Newton, M. D.; Pople, J. A. QCPE No. 236 (1970).

(28) Additionally, an orbital population analysis shows the exocyclic π bond to be slightly electron deficient.

6,6-Dimethylfulvene is thus seen to be an indicator substrate. The first of its kind, it readily differentiates electrophilic from nucleophilic carbene additions. Moreover, the observed regiochemistries of addition are nicely compatible with theoretical expectations. The overall result again demonstrates the power of combined experimental and theoretical analysis of carbenic reactivity.[30] We are continuing our studies of indicator substrates.

Acknowledgment. We are grateful to the National Science Foundation for financial support and the Center for Computer and Information Services of Rutgers University for computer time. We thank Professor K. D. Jordan for a helpful exchange of correspondence.

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(29) Additions of similarly stabilized carbenes (CF_2, CFOH, and $C(OH)_2$) to ethylene are calculated to have larger overlap at the transition state for $CXY^{HO}/alkene^{LU}$ interaction than for $CXY^{LU}/alkene^{HO}$ interaction.[6] These findings parallel our interpretation of the CH_3OCCl/**1** reaction. A perceptive referee has pointed out that because both interaction terms contribute to the endocyclic addition of CH_3OCCl, FMO theory might actually incorrectly predict this to be the favored mode of reaction, rather than the (observed) exocyclic addition, to which only the nucleophilic interaction can contribute. An extensive analysis of the reaction surface would be needed in order to locate the transition states and accurately evaluate the FMO interaction terms. This is calculationally impossible for systems as complicated as **1** and CH_3OCCl and would probably also stretch the applicability and accuracy of this approach beyond its limits. The transition state obtained in ref 6 for the model ambiphile HOCF adding to ethylene shows strong carbene interaction with one carbon of the ethylene. Analogously, the very large LUMO coefficient of C_6 of **1** may be the dominant factor in establishing large overlap at C_6 and thus controlling the regioselectivity of the CH_3OCCl addition to **1**.

(30) For a prior example, see: Moss, R. A.; Vezza, M.; Guo, W.; Munjal, R. C.; Houk, K. N.; Rondan, N. G. *J. Am. Chem. Soc.* 1979, *101*, 5088.

On the Heat Capacities of Activation for Displacements at Primary and Secondary Carbon Centers in Water

Michael Jesse Blandamer

Chemistry Department, University of Leicester
Leicester, United Kingdom

Ross Elmore Robertson

Chemistry Department, University of Calgary
Calgary, Alberta, Canada

Peter David Golding, Joseph Mark MacNeil, and
John Marshall William Scott*

Chemistry Department
Memorial University of Newfoundland
St. John's, Newfoundland, Canada

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The heat capacities of activation ($\Delta C_p^{\ddagger}$) related to solvolytic displacements in water

$$RX + 2H_2O \rightarrow ROH + H_3O^+ + X^- \qquad (1)$$

are invariably negative.[1] An analogy based on other ionogenic reactions in water, e.g., Brönsted acid-base reactions, provides a qualitative explanation for the above observation. Such a model leads to the reasonable conclusion that transition states related to the reactions summarized by eq 1 have considerable ionic character.

Some time ago Albery and Robinson[2] virtually discarded this model for the case RX = *tert*-butyl chloride. These authors postulated that the non-Arrhenius temperature dependence of the solvolytic rates arises as a consequence of an intermediate in the displacement reaction. Such a postulate is not uncongenial in the case of the tertiary center, but its wider application to primary and secondary substrates was considered to be incorrect.[3]

Table I. Rate and Temperature Data for the Hydrolysis of Ethyl Bromide

T, °C	$k \times 10^4$,[a] s^{-1}	$\Delta k \times 10^7$ [b]	k(I) × 10^4, s^{-1}	k(II) × 10^4, s^{-1}	k(III) × 10^4, s^{-1}
90.000	6.8313	4.04	6.8322	6.8314	6.8298
85.016	4.3503	5.13	4.3501	4.3496	4.3612
80.008	2.7252	4.82	2.7224	2.7221	2.7310
80.001	2.7230	4.08	2.7206	2.7203	2.7291
74.840	1.6493	2.08	1.6496	1.6494	1.6527
69.986	1.0117	0.58	1.0122	1.0121	1.0122
65.067	0.60518	0.56	0.60488	0.60480	0.60418
62.583	0.46255	0.46	0.46246	0.46240	0.46203
57.600	0.26463	0.26	0.26470	0.26467	0.26545

[a] The mean of 3-5 determinations, Δk is the standard deviation. [b] The Δk values were used as weighing factors in the Wentworth Regression; ΔT was fixed at 0.001 K for all temperatures. The k(I) and k(II) quantities were calculated from the two sets of values of A, B, C, and D appropriate to eq 7, and k(III) was obtained from the values of A, B, and C appropriate to eq 2. The number of significant figures given with respect to k, k(I), k(II), and k(III) is that required to calculate Ω to two significant figures.

Table II. Rate and Temperature Data for the Hydrolysis of *sec*-Propyl Methanesulfonate

T, °C	$k \times 10^4$,[a] s^{-1}	$\Delta k \times 10^7$ [b]	k(I) × 10^4, s^{-1}	k(II) × 10^4, s^{-1}	k(III) × 10^4, s^{-1}
32.520	5.0270	1.41	5.0251	5.0271	5.0249
30.001	3.6858	3.86	3.6889	3.6903	3.6919
30.007	3.6923	4.50	3.6916	3.6931	3.6946
27.502	2.7003	1.50	2.7011	2.7021	2.7044
25.007	1.9640	1.41	1.9640	1.9648	1.9665
22.007	1.3293	1.71	1.3291	1.3296	1.3304
70.005	1.0195	1.29	1.0189	1.1093	1.0195
17.496	0.72678	1.31	0.72570	0.72600	7.2575
14.997	0.51465	0.34	0.51389	0.51410	0.51371
12.495	0.36105	0.17	0.36102	0.36117	0.36084
10.003	0.25195	0.22	0.25199	0.25209	0.25193
7.510	0.17408	0.15	0.17440	0.17447	0.17454
4.997	0.11960	0.14	0.11928	0.11933	0.11961

[a] See footnote *a* of Table I. [b] See footnote *b* of Table I.

A decision between the Albery-Robinson approach and more traditional explanations for non-Arrhenius behavior in displacement reactions is nevertheless difficult, since the magnitude and general behavior of $\Delta C_p^{\ddagger}$ is conditioned largely by the assumptions which underpin its calculation from the rate-temperature (k-T) data. We recently have shown that the temperature dependence of the rates of hydrolysis of ethyl bromide and *sec*-propyl methanesulfonate demonstrate some features which are in agreement with the Albery-Robinson hypothesis.[4] This is of considerable interest, since the primary and secondary reactants in question are traditionally considered to be S_N2 or "borderline" substrates. In the present communication we reexamine the temperature dependence of the k-T data for the two substances mentioned above via the Valentiner equation

$$\ln k = A/T + B \ln T + C \qquad (2)$$

which considers $\Delta C_p^{\ddagger}$ to be real rather than anomalous (spurious[5]). Equation 2 also embodies all the "classical" notions concerning the origins of $\Delta C_p^{\ddagger}$ and tacitly assumes that the barrier to activation relates to a single step. In parallel, we also examine the k-T data for the same substances by using the Albery-Robinson

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(1) R. E. Robertson, *Prog. Phys. Org. Chem.*, **14**, 203 (1977). For an exception, see J. P. Barron, J. G. Winter, and J. M. W. Scott, *Can. J. Chem.*, **53**, 1051 (1975).

(2) J. Albery and B. H. Robinson, *Trans. Faraday Soc.*, **15**, 980 (1969).

(3) R. E. Robertson and J. M. W. Scott, *Can. J. Chem.*, **50**, 169 (1972).

(4) M. J. Blandamer, R. E. Robertson, J. M. W. Scott, and A. Vrielink, *J. Am. Chem. Soc.*, **102**, 2585 (1980).

(5) Both "spurious"[3] and "anomalous"[4] have been used to describe that part of the "heat capacity" which is postulated to derive from mechanistic complexity. See also S. Leung and E. Grunwald, *J. Phys. Chem.*, **74**, 687 (1970).

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