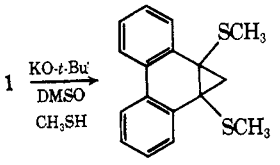
before it rearranged to the carbene. The result of this study is shown in eq 4. Compound **6**[7] almost

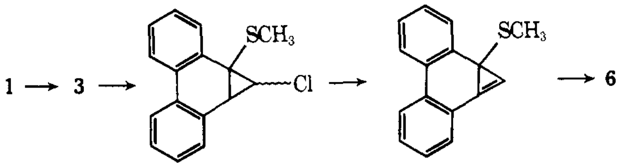


(4)

6

certainly arises by addition of the mercaptide to the cyclopropenes **3** and **8**[8] (Scheme III). The addition of

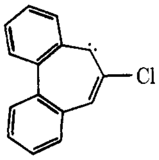
Scheme III



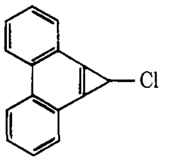
7 **8**

nucleophiles such as mercaptide and alkoxide to cyclopropene double bonds is well precedented in the work of Shields and Gardner[9] who have shown that these reactions are quite general.[10]

It is interesting that the cyclopropene **3** must be so unstable that it rearranges even at temperatures as low as 0° to give the arylcarbene, a species normally considered to be one of high energy. On the other hand, it must be sufficiently long-lived to experience addition of the nucleophile. The strain associated with **3** and the increase in resonance energy upon ring opening is probably sufficient to place the carbene at a lower energy than the cyclopropene. This is consistent with other examples of low temperature bicycloheptatriene → arylcarbene rearrangements.[1h] We did not observe insertion products arising from the cycloheptatrienylidene **9**, but this is not surprising since bicycloheptatriene → cycloheptatrienylidene rearrangements normally occur at much higher temperatures (250–600°). Another fate of **3** would be base-catalyzed isomerization to the cyclopropene **10**; however, this requires a cyclopropene



9



10

anion[11] intermediate which is probably too energetic to be formed under these conditions.

In conclusion, although this study does not provide any evidence which implicates bicycloheptatrienes in the arylcarbene → cycloheptatrienylidene rearrangements that have been reported,[1] we believe that the evidence provided for the discrete existence of such a species is rather compelling. Additional results in this area will be provided shortly in a full paper.

Acknowledgment. We gratefully acknowledge the Robert A. Welch Foundation and Eli Lilly Pharmaceutical Co. for support of this work.

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[7] Product **6**, mp 149–149.5°, was produced in 84% yield. Nmr (CCl_4) δ 1.21 and 1.80 (ABq, J_{AB} = 5.5 Hz, 2 H, cyclopropyl), 2.1 (s, 6 H, SCH_3), 7.1–7.6 (m, 2H, aromatic) and 7.9–8.7 (m, 1 H, aromatic), mass spectral 284.0688 (m^+), calcd 284.0692.

[8] The reaction was run with a sufficiently high concentration of KO-*t*-Bu and CH_3SH to minimize the formation of **7**. Experiments to trap the proposed bicycloheptatrienes with dienes are in progress.

[9] T. C. Shields and P. D. Gardner, *J. Amer. Chem. Soc.*, **89**, 5427 (1967).

[10] The regiospecificity of the addition of methylmercaptide to the cyclopropenes **3** and **8** is somewhat puzzling, since one might have expected that the anion would have added to give the more stable benzylic carbanion.

[11] R. Breslow, "Organic Reaction Mechanism," W. A. Benjamin, New York, N. Y., 1966, p 26.

[12] Alfred P. Sloan Foundation Fellow, 1973–1975.

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Activation Energies in Nucleophilic Displacement Reactions Measured at 296°K *in Vacuo*

Sir:

Recent theoretical studies[1,2] of the evolution of the energy of the reactants in several bimolecular nucleophilic displacement (SN2) reactions have inferred the presence of measurable activation energies. Computational difficulties have limited such studies to reactions proceeding *in vacuo*, *i.e.*, in the absence of solvent. Consequently, comparisons with experimental measurements made in solution, where solvation of either the nucleophile or the fragment ion in the transition state can raise or lower the activation energy, are of limited value. We wish to report in this communication experimental measurements of SN2 reactions made in the gas phase which allow, for the first time, direct comparisons with theoretical calculations. The experimental results are consistent with the prediction by theory[1,2] of energy barriers for the reactions

$$H^- + CH_3F \longrightarrow CH_4 + F^- \tag{1}$$

$$CN^- + CH_3F \longrightarrow CH_3CN + F^- \tag{2}$$

and also suggest the presence of energy barriers for several other SN2 reactions which may be amenable to calculation.

The experiments were performed in a flowing afterglow[3] and were of the type described previously.[4,5] The nucleophiles were all generated by the dissociative ionization of *ca.* 40 eV electrons: H^- and NH_2^- from NH_3 and CH_3NH_2, OH^- from H_2O, F^- from CF_4 and CH_3F, C_2H^- from C_2H_2, and CN^- from CH_3NH_2. Thermalization of the anions to the ambient room temperature of 296 ± 2°K prior to the reaction region was ensured by allowing the anions to undergo many thousands of collisions with the helium buffer gas molecules prior to their entry into the reaction region. The buffer gas was at a pressure of *ca.* 0.35 Torr. The methyl fluoride and methyl chloride reagent gases had minimum purities (liquid phase) of 99.0 and 99.5%, respectively. The measured rate constants which have an estimated[3] accuracy of ±20% are summarized in Tables I and II. Contributions to the rate constants

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[1] A. Dedieu and A. Veillard, *J. Amer. Chem. Soc.*, **94**, 6730 (1972).

[2] R. F. Bader, A. J. Duke, and R. R. Messer, *J. Amer. Chem. Soc.*, **95**, 7715 (1973).

[3] D. K. Bohme, R. S. Hemsworth, H. W. Rundle, and H. I. Schiff, *J. Chem. Phys.*, **58**, 3504 (1973).

[4] D. K. Bohme and L. B. Young, *J. Amer. Chem. Soc.*, **92**, 7354 (1970).

[5] L. B. Young, E. Lee-Ruff, and D. K. Bohme, *J. Chem. Soc., Chem. Commun.*, 35 (1973).

Table I. Rate Constants (in units of 10^{-9} cm^3 molecule^{-1} sec^{-1}) and Activation Energies for Exothermic Nucleophilic Displacement with CH_3Cl in the Gas Phase at 296°K

Nucleophile	$-\Delta H°_{298}$ kcal mol^{-1}	k_{exptl}[a]	k_{ADO}[b]	$k_{\mathrm{exptl}}/k_{\mathrm{ADO}}$	E_a,[c] kcal/mol^{-1}
H^-	86 ± 1	2.5[d]	8.5	0.29	0.7 ± 0.2
NH_2^-	66.1 ± 0.2	2.1[d]	2.4	0.88	0.1 ± 0.2
OH^-	49 ± 1	1.9[d]	2.4	0.79	0.1 ± 0.2
F^-	29 ± 8	1.8[d]	2.3	0.78	0.1 ± 0.2
C_2H^-	62 ± 2	1.2	2.1	0.57	0.3 ± 0.1
CN^-	30 ± 4 (15 ± 4)[e]	$\lesssim 0.0004$	2.0	$\lesssim 0.0002$	$\gtrsim 5$

[a] Unless indicated otherwise, the accuracy is ±20%. [b] Calculated using the average dipole orientation theory, ref 6. The adjustable parameter, $C = 0.21$. [c] See footnote 8. The uncertainty in E_a reflects only the uncertainty in k_{exptl}. [d] Reference 5. Accuracy is ±30%. [e] Production of isocyanomethane.

Table II. Rate Constants (in units of 10^{-9} cm^3 molecule^{-1} sec^{-1}) and Activation Energies for Exothermic Nucleophilic Displacement Reactions with CH_3F in the Gas Phase at 296°K

Nucleophile	$-\Delta H°_{298}$, kcal mol^{-1}	k_{exptl}[a]	k_{ADO}[b]	$k_{\mathrm{exptl}}/k_{\mathrm{ADO}}$	E_a,[c] kcal mol^{-1}
H^-	57 ± 8	0.015	7.6	0.0020	3.6 ± 0.1
NH_2^-	37 ± 9	0.017	2.3	0.0074	2.9 ± 0.1
OH^-	20 ± 8	0.024	2.2	0.011	2.6 ± 0.1
C_2H^-	33 ± 9	$\lesssim 0.0003$	2.0	$\lesssim 0.00015$	$\gtrsim 5$
CN^-	1 ± 11 (-14 ± 11)[d]	$\lesssim 0.0003$	2.0	$\lesssim 0.00015$	$\gtrsim 5$

[a] The accuracy is ±20%. [b] Calculated using the average dipole orientation theory, ref 6. The adjustable parameter $C = 0.23$. [c] See footnote 8. The uncertainty in E_a reflects only the uncertainty in k_{exptl}. [d] Production of isocyanomethane.

from the expected impurities in the reagent gases (CH_3Cl, SiF_4, and CH_3OCH_3 in the case of CH_3F and H_2O in the case of CH_3Cl) have been found to be negligible.

The reactions of H^-, NH_2^-, OH^-, F^-, and C_2H^- with CH_3Cl were all observed to proceed rapidly at essentially the theoretical capture rate[6,7] and consequently in the absence of any significant activation energy.[8] In contrast, the reaction with CN^- was observed to be surprisingly slow proceeding with a rate constant $k_{\mathrm{exptl}} \lesssim 0.0002k_{\mathrm{capture}}$. The formation of Cl^- is exothermic[9] in each case and was the only negative ion product observed. Although the neutral products were not identified, considerations of the energetics and mechanisms suggest that all the observed reactions correspond to nucleophilic displacement.[5]

The reactions of H^-, NH_2^-, OH^-, and C_2H^- with CH_3F were observed to be at least 100 times slower than the corresponding reactions with CH_3Cl. Indeed, for both the reactions of C_2H^- and CN^- the upper limit to k_{exptl} was measured to be 3×10^{-13} cm^3 molecule^{-1} sec^{-1} which corresponds to an activation energy of 5 kcal mol^{-1}.[8] F^- was the only product observed in all of these reactions with CH_3F which again should correspond to nucleophilic displacement.[10]

The recent calculations of Dedieu and Veillard[1] and Bader, *et al.*,[2] allow a direct comparison with the experimental results for reactions 1 and 2. The low reactivity of CN^- toward CH_3F was predicted by Bader, *et al.*,[2] whose calculations yield an overall activation energy of 22 kcal mol^{-1} for reaction 2. Such a large activation energy is not accessible to our room temperature measurements but the limit $E_a \gtrsim 5$ kcal mol^{-1} for reaction 2 implied by our present result is consistent with the theoretical prediction. However, the large uncertainty in $\Delta H°_{298}$ for reaction 2 does not rule out the possibility that the reaction is in fact endothermic by more than 5 kcal mol^{-1}. This is certainly the case if the CN^- ion is constrained by the electrostatic interaction during the collision to produce isocyanomethane. The accord between theory and experiment is much more pronounced for reaction 1 for which the *ab initio* LCAO-MO-SCF calculations of Dedieu and Veillard[1] predict a barrier of 3.8 cal mol^{-1} which is in remarkable agreement with the experimental value of 3.6 kcal mol^{-1}. Although this agreement may be fortuitous, the accord between theory and experiment generally for both SN2 reactions 1 and 2 is certainly very satisfying and should further encourage theoretical developments for reactions of this type. In particular, the origin of the energy barriers for the reaction of CN^- with CH_3Cl and of C_2H^- with CH_3F is especially intriguing.

Acknowledgment. We thank Professor Bader for calling our attention to the theoretical studies of SN2 reactions. The work was supported by the National Research Council of Canada.

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(6) T. Su and M. T. Bowers, *J. Chem. Phys.*, **58**, 3027 (1973) and *Int. J. Mass. Specrom. Ion Phys.*, **12**, 347 (1973).

(7) The polarizabilities and permanent dipole moments of CH_3F and CH_3Cl were taken from E. W. Rothe and R. B. Bernstein, *J. Chem. Phys.*, **31**, 1619 (1959).

(8) The activation energy, E_a, is calculated from the relationship $k_{\mathrm{exptl}} = k_{\mathrm{ADO}}e^{-E_a/RT}$. It is assumed that the reaction would proceed at the capture rate in the absence of an activation energy. The neglect of steric effects in this simple model is justified for this series of reactions (except in the *special* case of the CN^- reactions) to the extent that most of the CH_3Cl reactions proceed at the capture rate, indicating the absence of such effects. However, since there are reasons other than an energy of activation which can cause an observed rate constant to be lower than the capture rate constant, the value of E_a determined from this model must be rigorously regarded as a maximum.

(9) The heats of formation of the neutral species were taken from J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, "Ionization Potentials, Appearance Potentials, and Heats of Formation of Gaseous Ions," NSRD-NBS 26, U. S. Government Printing Office, Washington, D. C., 1969. The heats of formation of H^-, OH^-, F^-, and CN^- were taken from JANAF Thermochemical Tables, 2nd ed, *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand.*, **No. 37** (1971). $\Delta H_f°_{298}$ (NH_2^-) was taken from D. K. Bohme, R. S. Hemsworth, and H. W. Rundle, *J. Chem. Phys.*, **59**, 77 (1973) and $\Delta H_f°_{198}$ (C_2H^-) = 71 ± 1 kcal/mol, unpublished results from this laboratory.

(10) All other channels for the reactions of H^- and CN^- with CH_3F leading to the formation of F^- are endothermic. The presence of alternate channels for the C_2H^- reaction (several isomeric forms of CH_3C_2H are energetically accessible) would increase the lower limit to the activation energy deduced for the SN2 reaction. Both the NH_2^- and OH^- reactions have other channels leading to the formation of F^- which, within the uncertainty of $\Delta H°_{298}$, may be slightly exothermic but, as in the case of the CH_3Cl reactions,[5] are not likely to compete with the mechanistically simpler SN2 reaction.

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Detection of Neutral Products in Gas-Phase, Ion–Molecule Reactions

Sir:

Studies of ion–molecule reactions are relatively constrained, since, in contrast to most chemical investigations, the identity of only one of the products is usually determined.[1] In a majority of ion–molecule studies,

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(1) In some cases, neutral products may be inferred on the basis of product ion identity and energetics. For example, see J. L. Beauchamp, *Annu. Rev. Phys. Chem.*, **22**, 527 (1971).