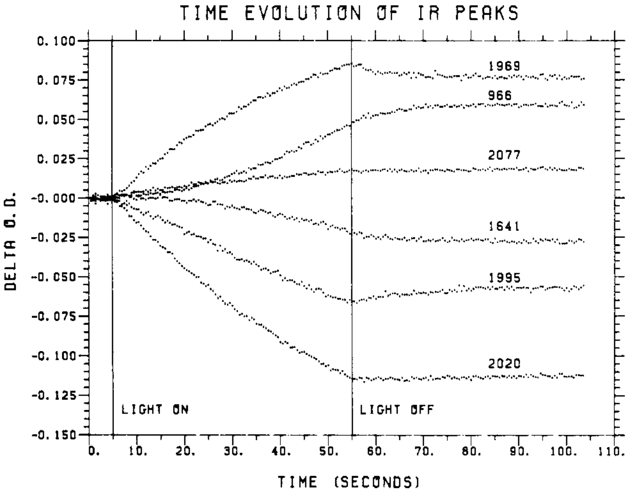

Figure 2. Time evolution of principal infrared bands before, during, and after irradiation of a mixture of $Fe(CO)_5$ and 1-pentene.

Both disappearance of 1-pentene and appearance of 2-pentene show an induction period suggesting that the active catalyst is not formed directly from pentacarbonyliron by a one-quantum process. The lifetime of the active catalytic species is determined by adding (with the proper signs) the absorption changes in both the olefin and carbonyl bands from the time the light is turned off to the end of the experiment. Ten seconds of the resulting composite trace is fit to an expression of the form $OD = C + A \exp(-Bt)$ where $1/B$ is taken as the catalyst life (assuming a first-order decay process). The measured lifetimes varied from 7 to 28 s and seem to depend most strongly on the concentration of 1-pentene present when the light is turned off. Thus the higher quantum yield observed in neat 1-pentene compared to dilute solutions[2] is more the result of longer catalyst life in this medium rather than a change in the intrinsic turnover rate.

The catalyst lifetime may be determined by olefin dissociation from (olefin)$Fe(CO)_3$ to give a fragment which rapidly decomposes to catalytically inactive species. At high concentrations of active catalyst such as might be produced by laser excitation, higher order kinetic processes might compete with the process found in this work.[5]

It is inappropriate to discuss quantum yields or catalyst cycles in these experiments, because the short path length in the IR cell allows most of the radiation to pass through unabsorbed and, at the low conversions studied, most of the pentacarbonyliron is only converted to the intermediate tetracarbonyl stage.

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Bridging the Gap between the Gas Phase and Solution: Transition in the Kinetics of Nucleophilic Displacement Reactions

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Now that techniques are available which allow the production of solvated ions in the gas phase, it has become possible to explore, in a quantitative manner, the transition in the kinetics and energetics of ion–molecule reactions from their solvent-free behavior to that observed in solution and so to deduce the absolute influence of solvent on such reactions.[1,2] Nucleophilic displacment reactions, for which we have shown that the specific rate can change by up to *20 orders of magnitude* in going from the gas phase to solution,[3] have received particular attention.[4,5] Here we report the first attempt to follow the transition in the kinetics of such reactions which ensues from the stepwise hydration of a nucleophile.[6] We have been able to follow this transition in the gas phase at room temperature for reaction 1 up to $n = 3$. The rate of this reaction in aqueous solution has been known for many years.[7]

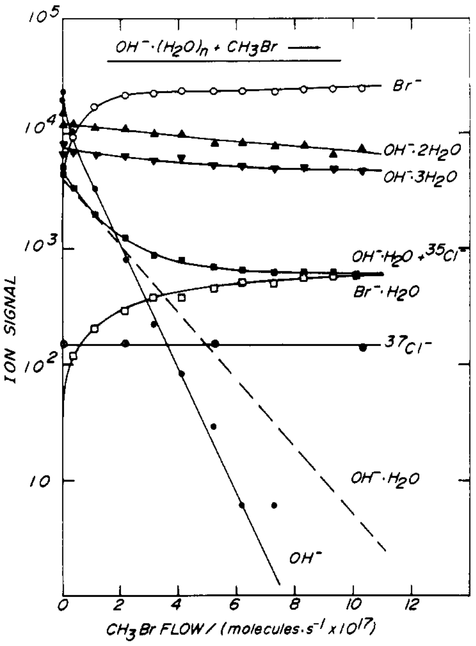

Figure 1. Variation of ion signals below m/e 100 recorded upon the addition of CH_3Br into a flowing H_2O/H_2 plasma in which unhydrated and hydrated hydroxide ions are initially present. The dashed curve represents the decay in $OH^-\cdot H_2O$ when account is taken of the contribution of $^{35}Cl^-$ to the measured m/e 35 signal. $P = 0.414$ torr, $T = 300$ K, $L = 60$ cm, $\bar{v} = 7.8 \times 10^3$ cm s^{-1}.

Table I. Room-Temperature Rate Constants Measured for Nucleophilic Displacement Reactions between Hydrated Hydroxide Ions and CH_3Br for Various Degrees of Hydration

hydroxide ion	rate constant
OH^-	$(1.0 \pm 0.2) \times 10^{-9}$ [a]
$OH^-\cdot H_2O$	$(6.3 \pm 2.5) \times 10^{-10}$
$OH^-\cdot(H_2O)_2$	$(2 \pm 1) \times 10^{-12}$
$OH^-\cdot(H_2O)_3$	$\leqslant 2 \times 10^{-13}$
$OH^-\cdot(H_2O)_n$	2.3×10^{-25} [b]

[a] In units of cm^3 molecule^{-1} s^{-1}. Each value represents the average of several measurements together with its estimated total accuracy. [b] In aqueous solution, from ref 7.

$$OH^-\cdot(H_2O)_n + CH_3Br \rightarrow Br^-\cdot(H_2O)_n + CH_3OH \quad (1)$$

The measurements were carried out by using the flowing-afterglow technique.[8] Hydroxide ions (~10 ppb) were generated

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(1) We have followed the influence of stepwise hydration on the kinetics of proton transfer from the hydronium ion to a variety of bases in the gas phase: Bohme, D. K.; Mackay, G. L.; Tanner, S. D. *J. Am. Chem. Soc.* **1979**, *101*, 3724.

(2) Equilibrium constant measurements carried out in our laboratory have provided insight into the transition from the gas phase to solution in the relative acidity of water and methanol: Mackay, G. I.; Bohme, D. K. *J. Am. Chem. Soc.* **1978**, *100*, 327.

(3) Tanaka, K.; Mackay, G. I.; Payzant, J. D.; Bohme, D. K. *Can. J. Chem.* **1976**, *54*, 1643.

(4) Olmstead, W. N.; Brauman, J. I. *J. Am. Chem. Soc.* **1977**, *99*, 4219.

(5) Pellerite, M. J.; Brauman, J. I. *J. Am. Chem. Soc.* **1980**, *102*, 5993.

(6) Early measurements carried out with the flowing-afterglow technique have shown that the rate of the gas-phase reaction of CH_3Cl with alkoxide ions is strongly decreased when the anion is solvated by one alcohol molecule: Bohme, D. K.; Brewster Young, L. *J. Am. Chem. Soc.* **1970**, *92*, 7354.

(7) Bathgate, R. H.; Moelwyn-Hughes, E. A. *J. Chem. Soc.* **1959**, 2642.

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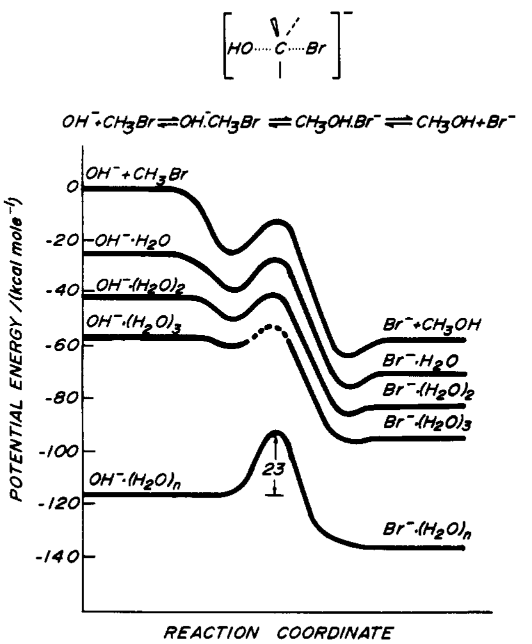

Figure 2. Possible semiquantitative reaction-coordinate profiles for the nucleophilic displacement reaction between OH^- and CH_3Br at various degrees of hydration. The total energies at infinite separation are based on known absolute heats of hydration,[12] and the barrier height ascribed to the transition state in aqueous solution has been taken to be equal to the measured activation energy.[7] The barrier heights ascribed to the transition state at intermediate degrees of hydration were chosen to be qualitatively consistent with the rate measurements reported in this study.

by electron impact on H_2O upstream in a flowing hydrogen plasma at total pressures of ca. 0.4 torr. The hydroxide ions were hydrated by reactions of type 2 and thermalized by collision in the H_2 bath

$$OH^-\cdot(H_2O)_n + H_2O + H_2 = OH^-\cdot(H_2O)_{n+1} + H_2 \qquad (2)$$

during the ~10 ms available prior to reaction downstream. Partial water vapor pressures were in the range 0.005–2 mtorr. The observations recorded at a fixed water vapor addition upstream and variable additions of CH_3Br into the reaction region are shown in Figure 1. Product ions of the type $Br^-\cdot(H_2O)_n$ with $n \geq 2$ were outside the range of detectability of the mass spectrometer. The data for several runs at various additions of water vapor[9] were analyzed to yield the rate constants summarized in Table I.

The rate constant for reaction 1 is seen to decrease progressively with the stepwise addition of water molecules up to $n = 3$ to a value which represents the present operational limit of our technique. The absolute efficiency of the solvent-free reaction may be estimated to be 0.4 from a comparison of the observed rate constant with the calculated collision rate constant.[10] The total drop in reactivity for hydration of the hydroxide ion up to $n = 3$ observed in the gas phase is almost 4 orders of magnitude. Aqueous solution measurements imply a futher drop in reactivity of 12 orders of magitude (see Table I).[7]

These striking results may be interpreted in terms of the qualitative model discussed by Brauman et al.[4,5] This model views reactions of this type to proceed in the three-step sequence (3)[11]

$$OH^-\cdot(H_2O)_n + CH_3Br \rightleftharpoons OH^-\cdot(H_2O)_n\cdot CH_3Br \rightleftharpoons CH_3OH\cdot(H_2O)_n\cdot Br^- \rightleftharpoons CH_3OH + Br^-\cdot(H_2O)_n \qquad (3)$$

which may be represented by potential-energy profiles with a double minimum as is done in Figure 2. The efficiency of reaction in the Brauman model results from the trade-off between two effects: (a) differences in entropies of activation between the formation of the transition state and its unimolecular decomposition back to reactants and (b) an energy barrier resulting from the differential solvation of the reactants and the transition state. The former effect is likely to be responsible for the slightly depressed efficiency observed in this study for the solvent-free reaction. The latter effect predominates in solution and accounts for the low reactivity in this medium. An inspection of the rate constants measured in the gas phase suggests that the energy associated with the reorganization of the solvent molecules (effect b) may already predominate at approximately $n = 2$, viz., the energy of the barrier associated with the potential-energy profile for $n = 2$ may be approximately equal to or slightly greater than the energy of the reactants. The observed rate (as well as the calculated reaction efficiency) drops by a factor of about 100 in going from $n = 1$ to $n = 2$ compared to a decrease of only a factor of about 2 in going from $n = 0$ to $n = 1$.

The absolute effect of solvent established by the measurements obtained in this study is likely to be representative of the solvent behavior of S_N2 reactions in general. The relative effects of different solvents which are so pronounced in solution should now also be amenable to measurement in the gas phase. We are therefore faced with the exciting prospect of elucidating a unified model of reactivity for nucleophilic displacement reactions proceeding in the gas phase and solution.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for financial support.

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[8] Bohme, D. K.; Hemsworth, R. S.; Rundle, H. W.; Schiff, H. I. *J. Chem. Phys.* **1973**, *58*, 3504.

[9] The initial relative population of the cluster ions, $OH^-\cdot(H_2O)_n$, was dependent on the amount of added water vapor. A wide range in the initial relative populations was desirable for the determination of the rate constants because of losses associated with the depletion of the source ion, $OH^-\cdot(H_2O)_{n-1}$.

[10] Efficiency is defined as the fraction of the collisions which result in reaction: efficiency = k_{obsd}/k_{coll}. The collision rate constant may be caluculated from the AADO theory: Su, T.; Su, E. C. F.; Bowers, M. T. *J. Chem. Phys.* **1978**, *69*, 2243.

[11] From a consideration of the overall energetics, it is conceivable that some solvent is "boiled off" according to

$$OH^-\cdot(H_2O)_n + CH_3Br \rightarrow Br^-\cdot(H_2O)_m + [(n - m)H_2O + CH_3OH]$$

In writing this reaction allowance has been made for the possible association of the water and methanol molecules.

[12] (a) Kebarle, P. *Annu. Rev. Phys. Chem.* **1977**, *28*, 445. (b) Kebarle, P. *Mod. Aspects Electrochem.* **1974**, *9*, 1–46.

Facile Synthesis, Spectral Characterization, and Ethylidene Transfer Reactions of Complexes of the Type $Cp(CO)(L)Fe{=}CHCH_3^+$

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Current routes to alkylcyclopropanes via intermolecular transfer of alkylcarbenes to alkenes are usually limited by low yields, in large measure due to competition from intramolecular rearrangements of the carbene or carbenoid. These isomerizations include, for example, 1,2-hydrogen or -alkyl migrations to give alkenes and insertions into γ and more remote C–H bonds to form cycloalkanes.[1,2] Observations by Casey[3] and Rosenblum[4] that

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[1] For summaries see: (a) Kirmse, W. "Carbene Chemistry", 2nd ed.; Academic Press: New York, 1971. (b) Jones, M.; Moss, R. A. *Carbenes* **1973**, *1*, 1–125.

[2] (a) Simmons, H. E.; Blanchard, E. P.; Smith, R. D. *J. Am. Chem. Soc.* **1964**, *86*, 1347–1356. (b) Newman, R. C. *Tetrahedron Lett.* **1964**, 2541. (c) Kirmse, W. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 891. (d) Kirmse, W.; Wachterhauser, G. *Tetrahedron* **1966**, *22*, 73–80. (e) The best previously reported procedure for transfer of ethylidene involves use of CH_3CHI_2/$(CH_3CH_2)_2Zn$: Nishimura, J.; Kawabata, N.; Furukawa, J. *Tetrahedron* **1969**, *25*, 2647–2659. (f) Kawabata, N.; Yamagishi, N.; Yamashita, S. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 466–468.

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