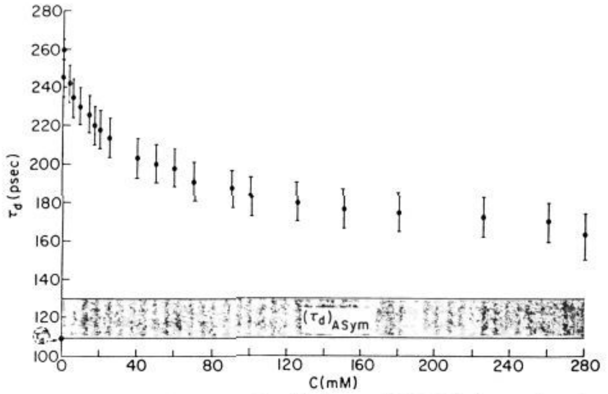

Figure 2. Average deprotonation lifetimes of HPTS (τ_d) as a function of $NaNO_3$ concentration. τ_d^m is the initial deprotonation lifetime found by direct measurements and $(\tau_d)_{asymp}$ is the theoretical lower limit for τ_d attainable by the salt effect.

these conditions the relative fluorescence efficiencies of the acid and base bands are directly proportional to the average deprotonation lifetime of the acid.[16,17,19]

$$\tau_d = \tau_f^{R^*OH}(\phi_{R^*OH}/\phi_{R^*O^-}) \qquad (1)$$

$\tau_d = (k_d)^{-1}$ is the average lifetime of the reaction

$$R^*OH \xrightarrow{k_d} R^*O^- + H^+$$

$\tau_f^{R^*OH}$ is the radiative lifetime of the excited acid (R^*OH) in the absence of proton dissociation, and ϕ_{R^*OH} and $\phi_{R^*O^-}$ are the absolute quantum yields of the acid and base forms, respectively. τ_d can be shown to be of a form of

$$\tau_d = \tau_d^m + \tau_d^{gem} \qquad (2)$$

τ_d^m is the pure dissociation lifetime of the molecule, which depends on the chemical properties of both the molecule and the solvent, and τ_d^{gem} is the geminate recombination contribution to the total dissociation lifetime, which is mainly dependent on the electrostatic interaction between the ion pair. In the asymptotic event where all the coulombic interaction is screened there is still a slight probability for a geminate encounter between the ions. For HPTS this asymptotic value is equal to $1.08\tau_d^m$; Introducing the value found by PTRS at 20 °C of $\tau_d^m = 110 \pm 10$ ps[3,7,12] one gets for the minimum deprotonation lifetime of HPTS attainable by total coulombic screening $(\tau_d^{HPTS})_{asym} = 120 \pm 10$ ps.[20]

Figure 2 shows τ_d calculated according to eq 1 as a function of the $NaNO_3$ concentration. The data were extracted from at least 20 independent experiments such as portrayed in Figure 1.

The asymptotic value of τ_d is clearly approached as the concentration of $NaNO_3$ is raised. However, at roughly 0.2 M $NaNO_3$ τ_d seems to level off at a value of 170 ± 10 ps. At these electrolyte concentrations the activity of the aqueous solution is significantly lowered and τ_d^m starts to increase with the $NaNO_3$ concentration.[13] Thus, at this range of concentrations (0.2–0.3 M $NaNO_3$) the decrease in τ_d^{gem} is cancelled out by the increase in τ_d^m and hence their sum, τ_d, remains practically constant. Further increase in the electrolyte concentration will eventually cause an increase in τ_d.[13] (At 4 M $NaNO_3$ τ_d^m was measured by PTRS to be 300 ± 30 ps.[20]) At the concentration range where τ_d^m is a constant and τ_d is well characterized (0–0.1 M $NaNO_3$), a quantitative analysis of the screening effect is possible. This analysis is the subject of a subsequent paper.[20]

Preliminary PTRS results of the HPTS/$NaNO_3$ system point to the same conclusion, i.e., the addition of the salt enhances the average dissociation rate of the photoacid.[22]

In summary, we present here for the first time clear evidence that reversible proton geminate recombination processes affect macroscopic observables such as the relative fluorescence quantum yields of photoacids. By doing so, we resolve the long-standing discrepancy between direct and indirect measurements of dissociation lifetimes of photoacids.

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Transesterification in the Gas Phase: Transfer of a Solvent Molecule from Reactant to Product Ions

Susan Baer, Page O. Stoutland, and John I. Brauman*

Department of Chemistry, Stanford University
Stanford, California 94305-5080

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Ion molecule reactions in the gas phase differ significantly from those in solution due to the absence of solvation effects. Recently, attempts have been made to bridge this difference by comparing the gas-phase reactivity of single ions and those complexed to one or more "solvent" molecules. In particular, equilibrium studies of these systems have resulted in significant advances in our understanding of the energetics of ion-solvent interactions.[1] The dynamic effects, however, are less well understood.[2] For example, S_N2 reactions of solvated ions have been studied, but the major reaction products are unsolvated.[3] In this paper, we report one of the first examples of a nucleophilic displacement in which the solvent molecule is efficiently transferred from the reactant to the product ion.[4]

We have investigated a series of reactions of alkoxide–alcohol dimers with selected alkyl formates using Fourier transform ion cyclotron resonance (FT-ICR) spectrometry.[5] As shown in Table

$$RO^- \cdot\cdot HOR + H\overset{O}{\overset{\|}{C}}OR' \longrightarrow ROH \cdot\cdot {}^-OR' + H\overset{O}{\overset{\|}{C}}OR \qquad (1)$$

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(4) There are scattered reports in the literature in which similar reactions have been observed. For example, see: (a) Hayes, R. N.; Paltridge, R. L.; Bowie, J. H. *J. Chem. Soc., Perkin Trans. II* **1985**, 567. (b) van der Wel, H.; Nibbering, N. M. M. *Recl. Trav. Chim. Pays-Bas* **1988**, *107*, 491.

(5) Experiments were performed with an IonSpec FTMS2000 mass spectrometer attached to a home-built vacuum system. Ions were trapped in a 1-in. cubic cell placed between the poles of an electromagnet operating at 10–12 kg. Ions were typically trapped for 1 s with the total gas pressures being ca. 10^{-6} Torr. All alkoxide ions except for unlabeled methoxide were generated from electron impact on the corresponding alkyl nitrites. Unlabeled methoxide was formed from electron impact on dimethyl peroxide. All reactant ions were isolated by standard notched ejection techniques. Reactions of the isolated ions with the neutral formates followed good pseudo-first-order kinetics.

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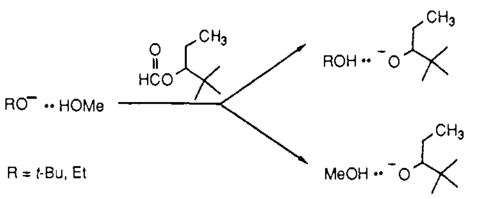
I, the reaction appears to be general, with the reactivity changing only for very bulky alkyl groups. Reactions involving smaller alkoxides (such as $^-$OMe) are ca. 20% efficient. The presence of bulky groups in either the dimer or the formate are observed to slow down the reaction. When any reaction is observed, only the solvated product is found. The reaction thermodynamics require transacylation with the solvent being transferred to the product ion as the reaction pathway.[6] Transacylation with solvent loss is endothermic by the alkoxide·alcohol solvation energy.

In order to better understand how the solvating alcohol affects the reactivity of the alkoxide, we have investigated the reaction of mixed dimers, [ROHOR′$^-$], with alkyl formates, HCOOR″. The dimer's structure should resemble the less basic alkoxide solvated by the less acidic alcohol,[8] for example [t-BuO$^-$·HoMe]. Two reaction products are possible: [ROHOR″]$^-$ and [R′OHOR″]$^-$. As shown below, the asymmetry present in the initial dimer is not reflected in the products; in almost all cases, close to equal amounts of the two products are observed. This suggests that the less basic alkoxide and the more basic alkoxide attack the formate with equal case. The initial solvent molecule is, thus, not merely a spectator; the distinction between solute and solvent is lost in the course of the reaction.

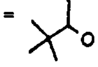


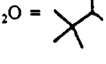
The results obtained from the mixed dimers (eq 6 and 7) show that the transition states for transfer of either alcohol from asymmetric dimers must have the same energy. This suggests that the negative charge of the initial alkoxide ion has been substantially dissipated at the transition state. The energetic equivalence of the two possible tetravalent species for the reaction of [t-BuO$^-$·HOMe] with $HCO_2CH(CH_2CH_3)C(CH_3)_3$ is not unexpected. The hydrogen bond strengths in the gas phase are attenuated relative to the acidity of the solvent alcohol,[9,10] and the only other difference (the *tert*-butyl group vs the methyl group) is four bonds away from the negative charge. In contrast, for separated ions, the energy required to transfer the proton from the more basic alkoxide to the less basic will require an energy which is the difference in acidities of the two alcohols (in this case, ca. 6 kcal/mol).

Equilibrium studies have shown the strength of the alcohol–alkoxide interaction[8,10] to be ca. 25 kcal/mol. One might expect that the solvent alcohol would remain coordinated to the site of negative charge at all times, thereby retaining the full 25 kcal/mol solvation energy. Recent results, however, suggest that some unsolvated tetrahedral adducts are unusually stable.[4b,11] Thus, there may be enough energy released upon formation of a tetrahedral species to break the hydrogen bond, leaving the solvent loosely coordinated to the anion. This loosely bound ion–dipole complex would be higher in energy than the hydrogen-bonded structure, but it may be energetically accessible. Therefore, it is possible that transfer of the solvent to the negative charge on the carbonyl oxygen does not proceed synchronously with addition of the alkoxide.

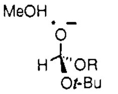
Table I. Transacylation Reactions[a]

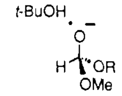
$MeOHO^*Me^- + HCOO^*Me$	→	$^*MeOHO^*Me^-$ (+ HCOOMe)	(1)
$MeOHO^*Me^- + HCOOMe$	→	$MeOHOMe^-$ (+ $HCOO^*Me$)	(2)
$MeHOMe^- + HCOO^*Me$	→	$MeHO^*Me^-$ (+ HCOOMe)	(3)
$MeOHOH^- + HCOOMe$	→	$MeOHOMe^-$ (+ HCOOH)	(4)
$MeOHOEt^- + HCOOEt$	→	$EtOHOEt^-$ + (+ HCOOMe)	(5)
$MeOHOEt^- + HCOOR_1$	→	$MeOHOR_1^-$ (+ HCOOEt) ~ 40%	(6)
	→	$EtOHOR_1^-$ (+ HCOOMe) ~ 60%	
$MeOHO$*t*-$Bu^- + HCOOR_1$	→	$MeOHOR_1^-$ (+ HCOO*t*-Bu) ~ 50%	(7)
	→	*t*-$BuOHOR_1^-$ (+ HCOOMe) ~ 50%	
$MeOHOR_2^- + HCOOR_1$	→	$MeOHOR_1^-$ (+ $HCOOR_2$)	(8)
	→	$R_2OHOR_1^-$ (+ HCOOMe)	
$MeOHOR_1^- + HCOOEt$	→	$EtOHOR_1^-$ (+ HCOOMe)	(9)
	→	$MeOHOEt^-$ (+ $HCOOR_1$)	
$MeOHOR_1^- + HCOOR_1$	→	$R_1OHOR_1^-$ (+ HCOOMe)	(10)
$MeOHOR_3^- + HCOOR_3$	→	$R_3OHOR_3^-$ (+ HCOOMe)	(11)
t-$BuOHOR_1^- + HCOOR_1$	→	$R_1OHOR_1^-$ (+ HCOO*t*-Bu)	(12)

[a] $^*MeO = {}^{13}CH_3O$, R_1O = 

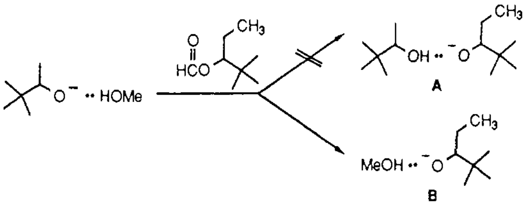
, R_2O = 

, $R_3O = PhCH_2O$.





Several dimer-formate reactions were not observed, namely those involving transfer of a large solvent (alcohol) molecule. Interestingly, attack by a large alkoxide, albeit very slow, can be observed. Product A is the product of attack by MeO$^-$ and transfer of the large alcohol, $(CH_3)_3CCH(CH_3)OH$; although thermodynamically favored, it is not observed. The observed product, B, on the other hand, is produced by attack of the larger alkoxide $(CH_3)_3CCH(CH_3)O^-$ and transfer of the smaller alcohol, MeOH. Other similar examples, where no reaction is observed, are shown in Table I.



In summary, this is an important example of a solvated gas-phase reaction in which the solvent is efficiently transferred from reactant to product. The presence of only one solvent molecule has been shown to affect the reaction outcome significantly. Further investigations of the effect of solvent on reactivity are underway.

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(6) A variant of the Riveros reaction is the only alternative mechanism:

$$[CH_3O^-{\cdot}HOCH_3] + HC({=}O)OCH_3 \rightarrow [CH_3O^-{\cdot}HOCH_3] + CO + HOCH_3$$

This possibility can be ruled out, however, due to its endothermicity, $\Delta H° = +9.2$, calculated using known heats of formation: Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley: New York, 1976. Formates with a deuterium in the acyl position react to give some incorporation of deuterium into the ionic product. This suggests the possibility of a modified Riveros reaction in which acyl proton abstraction from the formate is followed by decarbonylation, alkoxide–alcohol exchange, and recarbonylation to give a new formate ester (all of this occurring in the ion-molecule complex). Observation of transacylation reactions with alkyl esters,[4b,7] however, suggests that formate deprotonation is not required for transacylation.

(7) The reaction of methoxide·methanol with ethyl pivalate results in the formation of ethoxide·methanol. Baer, S.; Stoutland, P. O., unpublished results.

(8) Moylan, C. R.; Dodd, J. A.; Han, C.-C.; Brauman, J. I. *J. Chem. Phys.* **1987**, *86*, 5350.

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(10) There is some controversy surrounding the exact value for methanol–methoxide. See: (a) Caldwell, G.; Rozeboom, M. D.; Kiplinger, J. P.; Bartmess, J. E. *J. Am. Chem. Soc.* **1984**, *106*, 4660. (b) Meot-Ner, M.; Sieck, L. W. *J. Phys. Chem.* **1986**, *90*, 6687. (c) Meot-Ner, M.; Sieck, L. W. *J. Am. Chem. Soc.* **1986**, *108*, 7525. (d) Moylan, C. R.; Dodd, J. A.; Brauman, J. I. *Chem. Phys. Lett.* **1985**, *118*, 38.

(11) Reaction of $MeOHOMe^-$ with CF_3CO_2Me results in formation of $[CF_3CO(OMe)_2]^-$ + MeOH. For this to be observed, formation of the adduct from $MeO^- + CF_3CO_2Me$ must be exothermic by at least the hydrogen bond strength in $MeOHOMe^-$ (ca. 25 kcal/mol). Baer, S.; Stoutland, P. O. Unpublished results. See also ref 4b.