Formation, Reactivity, and Relative Stability of Clustered Alkoxide Ions by Ion Cyclotron Resonance Spectroscopy

Larry K. Blair, Paulo C. Isolani, and José M. Riveros*

Instituto de Quimica, University of São Paulo,
São Paulo, Brazil. *Received July 19, 1972*

Abstract: Ion cyclotron resonance spectroscopy has been used to study the general gas-phase reaction of alkoxide ions (R_aO^-) with alkyl formates ($HCOOR_b$) for R = CH_3, C_2H_5, and i-C_3H_7. These systems are shown to lead in all cases to the formation of a complex ion, $(R_aR_bO_2H)^-$, and to produce alkoxide displacement (R_bO^-) only when the electron affinity of $R_bO\cdot$ is equal to or larger than that of $R_aO\cdot$. Evidence is presented that the complex ions correspond to alkoxide ions "solvated" by a single neutral molecule of alcohol and presumably held by hydrogen bonding. The "solvated" alkoxide ions can react further with alcohols to establish the intrinsic clustering ability of alcohols by the formation of a preferential "solvated" species. The order of solvating ability is shown to follow the scale of gas-phase acidity, t-C_4H_9OH > i-C_3H_7OH > C_2H_5OH > CH_3OH.

Ion cyclotron resonance spectroscopy (icr) has been successfully used in gas-phase studies of ion–molecule reactions to point out the importance of solvent effects in determining reactivity in solution. For example, the acidity order of simple alcohols in the gas phase is the reverse of the order in solution.[1,2] Likewise, the acidities of the hydrocarbons toluene and propylene are greater than the acidity of water in the gas phase.[3] The basicities of the amines follow the order $(CH_3)_3N > (CH_3)_2NH > CH_3NH_2 > NH_3$, whereas the solution order does not obey this simple trend.[4] Since equilibria and kinetics are generally complex functions of intrinsic effects and solvation, these studies are particularly relevant for the separation of these factors and the understanding of the correct relationship between structure and reactivity.

This paper reports the application of icr to a new and unique method for the indirect preparation of gas-phase alkoxide ions, "solvated" by a single neutral molecule of alcohol. This method is based on the general gas-phase reaction of alkoxide ions with alkyl formates in the pressure range of 10^{-6} to 5×10^{-5} Torr, where bimolecular collisions are the only important processes. The "solvated" alkoxide ions thus formed can be further reacted with other neutral molecules to establish the order of preference of neutrals as solvating agents. In this study, the relative order of intrinsic solvating ability of the simple alcohols is determined by icr and related to hydrogen-bonding ability.

The trend observed for relative stability of "solvated" species parallels closely the extensive measurements recently carried out by high-pressure mass spectrometry on gas-phase ionic equilibria of Cl^- solvated by different hydrogen-bonding neutrals.[5] Furthermore, the relationship established in ref 5 by Kebarle between gas-phase acidity and the hydrogen-bonding capability of the "solvent" molecule is further explored for the case of the simple alcohols.

Experimental Section

All the experiments were carried out in a Varian V-5900 icr spectrometer provided with a dual inlet system. The pressure readings quoted throughout this work (10^{-6} to 5×10^{-5} Torr) were obtained from the VacIon current and should therefore be regarded as approximate values. A typical flat cell design[6] was found to be satisfactory for the present study. Double-resonance experiments were carried out in the usual fashion,[7] maintaining low ion currents and low irradiating fields.[8]

The alkoxide ions were generated by electron impact of alkyl nitrites at 20 eV.[9] The production of minor quantities of HNO^- and NO_2^- did not interfere with the reactions reported below. The NO_2^- intensity could be appreciably reduced by storing the nitrites at low temperatures and pressures in glass bulbs wrapped in aluminum foil. The nitrites themselves were prepared by alcoholysis of isoamyl nitrite and purified by fractional distillation.

The alkyl formates and alcohols were of reagent grade quality, and deuterated alkyl formates and alkyl nitrites were prepared from the corresponding deuterated alcohols (Merck). The purity of all reagents was checked by a combination of gc, nmr, and low-pressure icr.

The reactivity of the solvated alkoxide ions was studied by bleeding into the cell an approximately 1:2 mixture of alkyl (R_a) nitrite and alkyl (R_b) formate, and varying the amounts of the reacting neutrals through different inlets.

Results

A. General Reactions of Alkoxide Ions with Alkyl Formates. The reactions taking place in the cell of an icr spectrometer in the pressure range of 10^{-6} to 5×10^{-5} Torr can be divided into two cases depending on the relative size of the alkyl groups involved in the system.

(1) For $R_a > R_b$

$$R_aO^- + HCOOR_b \longrightarrow (R_aR_bO_2H)^- + CO \qquad (1)$$

The actual systems investigated in this category were the following: $C_2H_5O^- + HCOOCH_3$, i-$C_3H_7O^- + HCOOC_2H_5$, i-$C_3H_7O^- + HCOOCH_3$, $C_2H_5O^- + HCOOCD_3$, i-$C_3H_7O^- + HCOOCD_3$.

For these cases, the only new feature observed in the negative-ion icr spectrum is an intense peak corresponding to a complex ion of mass number equal to the sum of the masses of the two reactants minus 28 mass units (Figure 1). Double-resonance studies, as well as pressure dependence of these high mass peaks, indicate that this complex ion does in fact come from the general reaction of an alkoxide ion with the corresponding

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(1) J. I. Brauman and L. K. Blair, *J. Amer. Chem. Soc.*, **90**, 6561 (1968).

(2) J. I. Brauman and L. K. Blair, *ibid.*, **92**, 5986 (1970).

(3) J. I. Brauman and L. K. Blair, *ibid.*, **93**, 4315 (1971).

(4) J. I. Brauman, J. M. Riveros, and L. K. Blair, *ibid.*, **93**, 3914 (1971).

(5) R. Yamdagni and P. Kebarle, *ibid.*, **93**, 7139 (1971).

(6) J. L. Beauchamp, Ph.D. Thesis, Harvard University, 1967, Appendix 1.

(7) L. R. Anders, J. L. Beauchamp, R. C. Dunbar, and J. D. Baldeschwieler, *J. Chem. Phys.*, **45**, 1062 (1966).

(8) G. C. Goode, A. J. Ferrer-Correia, and K. R. Jennings, *Int. J. Mass Spectrom. Ion Phys.*, **5**, 229 (1970).

(9) K. Jager and A. Henglein, *Z. Naturforsch. A*, **22**, 700 (1967).

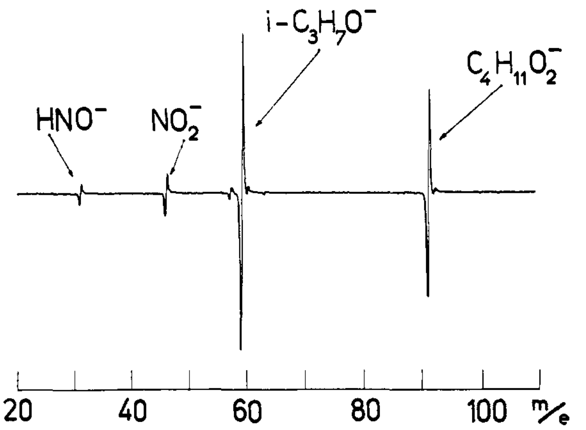

Figure 1. Negative ion spectrum of an approximately equimolar mixture of isopropyl nitrite and methyl formate at 1 × 10^{-5} Torr. The ion at *m/e* 91 corresponds to $i\text{-}C_3H_7O^-(CH_3OH)$.

alkyl formate. No other appreciable products of ion-molecule reactions are observed in these mixtures in the indicated pressure range. A special situation arises when ethyl nitrite is used as the source of negative ions, as both $C_2H_5O^-$ (*m/e* 45) and $C_2H_3O^-$ (*m/e* 43) are produced in appreciable quantities. Addition of methyl formate only yields a complex ion of mass 77.

(2) **For $R_a \leq R_b$.** The complex ion produced by reaction 1 appears again as a strong feature in the negative-ion icr spectrum. Unlike the cases previously considered, the production of R_bO^- by a formal alkoxide displacement is also observed as a product.

$$R_aO^- + HCOOR_b \longrightarrow R_bO^- + HCOOR_a \tag{2}$$

By increasing the pressure of $HCOOR_b$ relative to the nitrite, tertiary products are observed in these cases corresponding to the complex ion of reaction 1, but produced by R_bO^- and $HCOOR_b$ (Figure 2). The following systems were investigated in this category: $i\text{-}C_3H_7O^- + HCOOCH(CH_3)_2$, $CH_3O^- + HCOOCD_3$, $CD_3O^- + HCOOCH_3$, $i\text{-}C_3H_7O^- + HCOOCH(CD_3)_2$, $C_2D_5O^- + HCOOC_2H_5$, $CH_3O^- + HCOOC_2H_5$, $CD_3O^- + HCOOC_2H_5$, $CH_3O^- + HCOOCH(CH_3)_2$, $C_2H_5O^- + HCOOCH(CH_3)_2$, $CD_3O^- + HCOOCH(CD_3)_2$, and $CH_3O^- + HCOOC_3H_7$.

Although no rigorous kinetic treatments have been carried out for each individual case, the extent of the competitive reactions 1 and 2 is dependent on the system. Thus, both reactions proceed at comparable rates for the case of $CH_3O^- + HCOOCH(CH_3)_2$. On the other hand, where $R_a = R_b$, reaction 1 is favored, and for the extreme case of $CH_3O^- + HCOOC_6H_5$ reaction 2 is the only product observed.

B. Structure of the Complex Ion. From a consideration of mass alone, the neutral fragment of mass 28 lost in the formation of the complex must be either CO or C_2H_4. The consistent loss of mass 28 with variation of the alkyl group structure provides strong evidence that CO is the expelled neutral fragment. In this respect, the reaction

$$\underset{m/e\ 34}{CD_3O^-} + HCOOCH(CD_3)_2 \longrightarrow \underset{m/e\ 100}{\text{complex ion}} + \text{neutral}$$

and the subsequent reaction of

$$\underset{m/e\ 65}{(CD_3)_2CHO^-} + HCOOCH(CD_3)_2 \longrightarrow \underset{m/e\ 131}{\text{complex ion}} + \text{neutral}$$

where C_2H_4 cannot be lost, are particularly conclusive in identifying the neutral as CO. Thus, the complex formation is actually an alkoxide induced decarbonylation of an alkyl formate. This reaction is similar to the well-known decarbonylation of alkyl formates by strong base.[10]

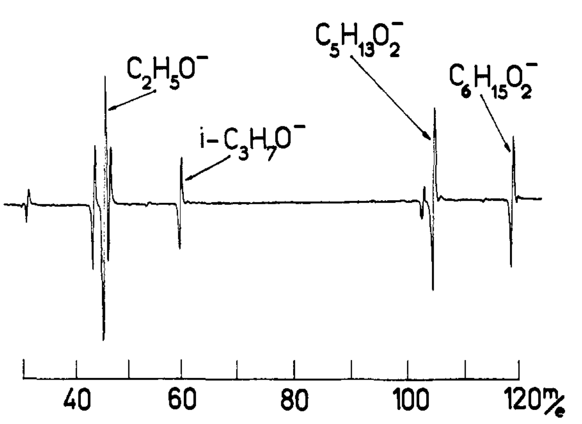

Figure 2. Negative ion spectrum of an approximately 2:1 mixture of isopropyl formate and ethyl nitrite at 2 × 10^{-6} Torr. The ion at *m/e* 105 corresponds to $i\text{-}C_3H_7O^-(C_2H_5OH)$, whereas the ion at *m/e* 119 is a tertiary ion produced from the reaction of $i\text{-}C_3H_7O^-$ and $HCOOCH(CH_3)_2$.

Although the structure of the complex is not directly observable, some definite conclusions can be reached on the nature of this species which has the formal composition of an alkoxide ion clustered by a single molecule of alcohol, namely $(R_aO \cdot R_bOH)^-$.

The complex ion formed from the reaction of CH_3O^- (*m/e* 31) + $HCOOCH(CH_3)_2$ and that formed from $(CH_3)_2CHO^-$ (*m/e* 59) + $HCOOCH_3$, with formal composition $[(CH_3)_2CHO \cdot CH_3OH]^-$ (*m/e* 91), have identical reactivity.

At pressures higher than 10^{-5} Torr, the complex ion of mass 91 reacts with C_2H_5OH to yield exclusively a new complex ion of *m/e* 105 in both cases. Double-

$$\underset{m/e\ 91}{(C_4H_{11}O_2)^-} + C_2H_5OH \longrightarrow \underset{m/e\ 105}{(C_5H_{13}O_2)^-} + CH_3OH \tag{3}$$

resonance experiments and pressure-dependence studies confirm this reaction. Similar behavior is observed for other pairs of R_a and R_b, indicating that the structure of the complex ion depends only on R_a and R_b, but that it is immaterial whether these groups are contained in the reactant ion or neutral.

A more valuable piece of information can be extracted from the experiment where the ion $[(CH_3)_2CHO \cdot CD_3OH]^-$ (*m/e* 94), made from $(CH_3)_2CHO^-$ + $HCOOCD_3$, reacts with C_2H_5OH *exclusively* by reaction 4. Thus, no scrambling takes place between the

$$\underset{m/e\ 94}{(C_4H_8D_3O_2)^-} + C_2H_5OH \longrightarrow \underset{m/e\ 105}{(C_5H_{13}O_2)^-} + CD_3OH \tag{4}$$

hydrogens and the deuteriums of the original alkyl groups, R_a ($i\text{-}C_3H_7$) and R_b (CD_3).

For the case where R_a and R_b are chemically equal, the complex thus formed can be reacted with an appropriate alcohol, R_cOH, to yield comparable quantities[11] of $(R_aOR_cOH)^-$ and $(R_bOR_cOH)^-$. Such a behavior was encountered in reactions 5–7.

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[10] J. C. Powers, R. Seidnar, and T. G. Parson, *Tetrahedron Lett.*, 1713 (1965).

[11] Equal quantities of the products are not observed in reactions 5 and 7 because an appreciable and consistent isotope effect favors the substitution of the deuterated "solvent" molecule by roughly a factor of 1.3. Such an effect is not observed in reaction 6 where no α deuteriums are present.

Table I. Reactivity of Clustered Alkoxide Ions, $R_aO^-(R_bOH) + R_cOH$

$R_a > R_c > R_b$

$i\text{-}C_3H_7O^-(CD_3OH) + C_2H_5OH \rightarrow i\text{-}C_3H_7O^-(C_2H_5OH) + CD_3OH$
$i\text{-}C_3H_7O^-(CH_3OH) + C_2H_5OH \rightarrow i\text{-}C_3H_7O^-(C_2H_5OH) + CH_3OH$
$i\text{-}C_3H_7O^-(CD_3OH) + C_2D_5OD \rightarrow i\text{-}C_3H_7O^-(C_2H_5OD) + CD_3OH$
$\rightarrow i\text{-}C_3H_7O^-(C_2D_5OH) + CD_3OD$
$i\text{-}C_3H_7O^-(CH_3OH) + C_2D_5OD \rightarrow i\text{-}C_3H_7O^-(C_2D_5OD) + CH_3OH$
$\rightarrow i\text{-}C_3H_7O^-(C_2D_5OH) + CH_3OD$

$R_a > R_c = R_b$

$i\text{-}C_3H_7O^-(CH_3OH) + CD_3OD \rightarrow i\text{-}C_3H_7O^-(CH_3OD) + CD_3OH$
$\rightarrow i\text{-}C_3H_7O^-(CD_3OH) + CH_3OD$
$\rightarrow i\text{-}C_3H_7O^-(CD_3OD) + CH_3OH$

$R_c > R_a, R_b$

$CH_3O^-(CD_3OH) + t\text{-}C_4H_9OH \rightarrow t\text{-}C_4H_9O^-(CH_3OH) + CD_3OH$
$\rightarrow t\text{-}C_4H_9O^-(CD_3OH) + CH_3OH$
$t\text{-}C_4H_9O^-(CH_3OH) + t\text{-}C_4H_9OH \rightarrow t\text{-}C_4H_9O^-(t\text{-}C_4H_9OH)$
$CH_3O^-(CD_3OH) + i\text{-}C_3H_7OH \rightarrow i\text{-}C_3H_7O^-(CH_3OH) + CD_3OH$
$\rightarrow i\text{-}C_3H_7O^-(CD_3OH) + CH_3OH$
$i\text{-}C_3H_7O^-(CH_3OH) + i\text{-}C_3H_7OH \rightarrow i\text{-}C_3H_7O^-(i\text{-}C_3H_7OH) + CH_3OH$
$i\text{-}C_3H_7O^-[(CD_3)_2CHOH] + t\text{-}C_4H_9OH \rightarrow t\text{-}C_4H_9O^-(i\text{-}C_3H_7OH) + (CD_3)_2CHOH$
$\rightarrow t\text{-}C_4H_9O^-[(CD_3)_2CHOH] + i\text{-}C_3H_7OH$
$t\text{-}C_4H_9O^-(i\text{-}C_3H_7OH) + t\text{-}C_4H_9OH \rightarrow t\text{-}C_4H_9O^-(t\text{-}C_4H_9OH) + i\text{-}C_3H_7OH$
$C_2H_5O^-(C_2D_5OH) + i\text{-}C_3H_7OH \rightarrow i\text{-}C_3H_7O^-(C_2H_5OH) + C_2D_5OH$
$\rightarrow i\text{-}C_3H_7O^-(C_2D_5OH) + C_2H_5OH$
$i\text{-}C_3H_7O^-(C_2H_5OH) + i\text{-}C_3H_7OH \rightarrow i\text{-}C_3H_7O^-(i\text{-}C_3H_7OH) + C_2H_5OH$

(a) Complex $(CH_3O \cdot CD_3OH)^-$ (*m/e* 66) formed either by $CH_3O^- + HCOOCD_3$ or $CD_3O^- + HCOOCH_3$.

$$\underset{m/e\ 66}{(C_2H_4D_3O_2)^-} + i\text{-}C_3H_7OH \left\{ \begin{array}{l} \rightarrow \underset{m/e\ 91}{(C_4H_{11}O_2)^-} + CD_3OH \\ \rightarrow \underset{m/e\ 94}{(C_4H_8D_3O_2)^-} + CH_3OH \end{array} \right. \quad (5)$$

(b) Complex $[i\text{-}C_3H_7O \cdot (CD_3)_2CHOH]^-$ (*m/e* 125) produced from $i\text{-}C_3H_7O^- + HCOOCH(CD_3)_2$.

$$\underset{m/e\ 125}{(C_6H_9D_6O_2)^-} + t\text{-}C_4H_9OH \left\{ \begin{array}{l} \rightarrow \underset{m/e\ 133}{(C_7H_{17}O_2)^-} + C_3D_6HOH \\ \rightarrow \underset{m/e\ 139}{(C_7H_{11}D_6O_2)^-} + C_3H_7OH \end{array} \right. \quad (6)$$

(c) Complex $(C_2D_5O \cdot C_2H_5OH)^-$ (*m/e* 96) produced from $C_2D_5O^- + HCOOC_2H_5$.

$$(C_4H_6D_5O_2)^- + i\text{-}C_3H_7OH \left\{ \begin{array}{l} \rightarrow \underset{m/e\ 105}{(C_5H_{13}O_2)^-} + C_2D_5OH \\ \rightarrow \underset{m/e\ 110}{(C_5H_8D_5O_2)^-} + C_2H_5OH \end{array} \right. \quad (7)$$

These experiments conclusively show that for the symmetrical reaction, *i.e.*, $R_a = R_b$, both groups are located in chemically equivalent positions within the complex ion. This evidence strongly suggests that the complex is in fact a "solvated" ion, an alkoxide-alcohol moiety.

For the simplest case, the structure of the "solvated" ion would be $(CH_3O \cdots H \cdots OCD_3)^-$, presumably held together by hydrogen bonding. Partial support for a hydrogen-bonded structure is also verified by the reaction of $i\text{-}C_3H_7O^-(CH_3OH)$ with CD_3OD, where besides the thermoneutral replacement of CH_3OH by CD_3OD in the complex, reaction 8 is observed to take place slowly as the pressure of CD_3OD is raised in the cell.

$$\underset{m/e\ 91}{(i\text{-}C_3H_7O \cdots H \cdots OCH_3)^-} + CD_3OD \longrightarrow \underset{m/e\ 92}{(i\text{-}C_3H_7O \cdots D \cdots OCH_3)^-} + CD_3OH \quad (8)$$

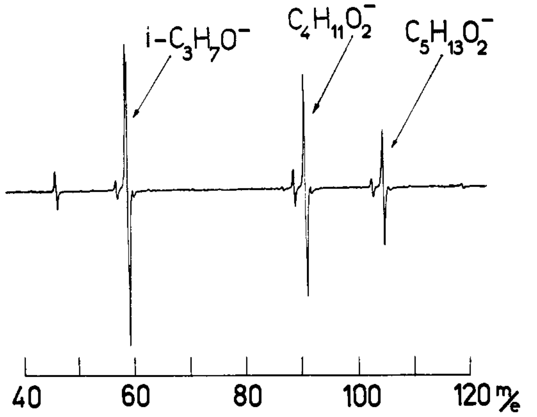

Figure 3. Negative ion spectrum at 4 × 10^{-5} Torr of approximately equal quantities of isopropyl nitrite, methyl formate, and ethanol. The only feature compared to Figure 1 is the formation of the ion $i\text{-}C_3H_7O^-(C_2H_5OH)$ by a "solvent" substitution reaction of the *m/e* 91 ion.

C. General Reactivity of Clustered Alkoxide Ions. In the previous section, it was shown that the solvated ions are capable of undergoing substitution of an alcohol moiety in the complex by another neutral molecule. These substitutions are observed in the 10^{-5} Torr region, and the characteristic specificity of such reactions indicate the preferred "solvent" molecule for a given ion. For example, the ion $i\text{-}C_3H_7O^-(CH_3OH)$ reacts with C_2H_5OH to yield exclusively $i\text{-}C_3H_7O^-(C_2H_5OH)$ and CH_3OH (reaction 3), rather than the other possible product ion and $i\text{-}C_3H_7OH$ (Figure 3). Likewise, the complex $(CH_3O \cdots H \cdots OCD_3)^-$ reacts with $i\text{-}C_3H_7OH$ to yield both $i\text{-}C_3H_7O^-(CH_3OH)$ and $i\text{-}C_3H_7O^-(CD_3OH)$ and the corresponding neutrals (reaction 5). When the pressure of $i\text{-}C_3H_7OH$ is increased both of these ions react further to yield the ion $i\text{-}C_3H_7O^-(i\text{-}C_3H_7OH)$.

The preferred order of substitution for several reactions investigated in the present case is listed in Table I. As these "solvent" displacement reactions are observed under conditions where the ions are trapped in the cell for only a few milliseconds, and thus far away from equilibrium, the observed reactions lead in a straightforward fashion to the following gas-phase "monosolvating" ability of alcohols: $t\text{-}C_4H_9OH > i\text{-}C_3H_7OH > C_2H_5OH > CH_3OH$.

Other related hydroxylic compounds and electron-deficient compounds like BF_3 can also be used as neutral reactants with the clustered species. For example, the reaction of $C_2H_5O^-(CH_3OH)$ with BF_3 shows no apparent preferential substitution specificity as reactions 9a and 9b proceed to approximately equal extent.

$$C_2H_5O^-(CH_3OH) + BF_3 \left\{ \begin{array}{ll} \longrightarrow (C_2H_5OBF_3)^- + CH_3OH & (9a) \\ \longrightarrow (CH_3OBF_3)^- + C_2H_5OH & (9b) \end{array} \right.$$

On the other hand, the clustered alkoxide ions are unreactive with respect to simple amines, and reaction with alkyl chlorides produces only Cl^- in a competitive process with the nude alkoxide ion, as previously reported for similar systems.[12] A similar behavior is observed in the reaction with C_2H_5SH, where the only observed product corresponds to $C_2H_5S^-$.

Discussion

The general gas-phase reaction between alkoxide ions and alkyl formates has been shown to yield two possible products: (1) the formation of an alkoxide–alcohol cluster and (2) formal alkoxide displacement in restricted cases.

The "solvated" alkoxide ions produced *via* decarbonylation of formates presumably arise from initial attack on the formyl hydrogen. The method is indeed a very convenient way of making clustered negative ions, as the direct association of R_aO^- and R_bOH is not observed in an icr spectrometer within its convenient pressure range for the simple alcohols. Furthermore, the fact that such a reaction is a fast one in the icr time scale enables the study of the reactivity of "solvated" species using the advantages of the icr technique as demonstrated in our case for the alcohols as solvent molecules. This reaction can also be used to form alkoxide ions "solvated" by a water molecule by reacting OH^- with an alkyl formate, or an alkoxide ion with HCOOH. However, in this case other reactive channels predominate and therefore have not been included in the present discussion.[13]

The trend obtained for the gas-phase "solvating" and hydrogen-bonding ability of a single molecule of alcohol by reactivity arguments, namely, $CH_3OH < C_2H_5OH < i\text{-}C_3H_7OH < t\text{-}C_4H_9OH$, is in general agreement with the relationship established by Kebarle[5,14] of increasing hydrogen-bond strength with gas-phase acidity. Such a trend can be explained by an extension of the polarizability arguments advanced by Brauman and Blair[1,2] to explain the stability of negative ions. Thus, the preferential formation of a larger complex by a given alkoxide ion can be explained by the presence of more polarizable matter (alkyl group) in the larger complex and partial delocalization of the net charge.[15] The actual hydrogen-bond strength of the alkoxide–alcohol clustered species should be in the vicinity of the 24 kcal/mol determined for the ion $(HO\cdots H\cdots OH)^-$ by high pressure mass spectrometry.[16] However, the bond strengths may actually be considerably higher if the dissociation energy of the $OH^-(H_2O)$ is actually closer to the 36 kcal/mol determined by Friedman.[17]

The alkoxide displacement reaction (eq 2) can be considered the gas-phase analog of a transesterification reaction. Although it is difficult to exclude completely the possibility that reactions 1 and 2 proceed *via* the same mechanism, with excited clustered ions decomposing to yield alkoxide ions, the absence of R_bO^- when $R_a > R_b$ seems to favor for the alkoxide displacement a more direct attack of the negative ion on the partially positive carbonyl carbon.[18]

The directional specificity of reaction 2 to yield the larger alkoxide ion is reminiscent of the results for the proton transfer in the system $R_aO^- + R_bOH \rightleftharpoons R_aOH + R_bO^-$, where the reaction is favored in the direction to yield the larger alkoxide ion.[1,2] The same analysis and interpretation made for the proton transfer studies can be applied to reaction 2. Thus, the energetics of the reaction

$$R_aO^- + HCOOR_b \longrightarrow R_bO^- + HCOOR_a$$

can be considered as the sum of the difference in the two C–O bond strengths of the alkyl formates, and the difference in electron affinities of the two alkoxyl radicals. If the C–O bond strengths are assumed to be approximately equal,[19] the ΔH for the alkoxide displacement will be determined by the relative electron affinities of the alkoxyl radicals. Thus, the experimental results for reaction 2 further support the evidence of Brauman and Blair[1,2] for the increase in electron affinity of the alkoxyl radicals with increasing alkyl substitution.

The systems reported here for the behavior of nude and "solvated" alkoxide ions in the gas phase in conditions suitable for icr studies and applications to similar systems should provide an important approach to understanding and bridging the relationship between intrinsic and solution reactivity.

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[16] J. D. Payzant, R. Yamdagni, and P. Kebarle, *ibid.*, **49**, 3308 (1971).

[17] M. DePaz, A. Guidoni Giardini, and L. Friedman, *J. Chem. Phys.*, **52**, 687 (1970).

[18] It is important to notice that if the alkoxide displacement reaction proceeds *via* excited complex ions, *i.e.*, $R_aO^- + HCOOR_b \rightarrow R_aOH + CO + R_bO^-$, the reaction for $R_a = R_b$, which is detected, would be endothermic by about 9 kcal/mol.

[19] P. Gray and A. Williams, *Chem. Rev.*, **59**, 239 (1959); J. A. Kerr, *ibid.*, **66**, 465 (1966). For the case of the acetates the C–O bond strength is essentially constant (within 1 kcal/mol) for the first alkyl groups, despite differences in the absolute values reflecting different values for the heat of formation of $CH_3CO\cdot$ and the alkoxyl radicals. For the case of formates, a rigorous analysis is complicated by the lack of accurate data, except for methyl formate; see J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, and K. Draxl, *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand.*, **26**, 268 (1969).