3.50 (J_{PH} = 8.5; J_{HH} = 7 Hz, methylene hydrogens of the ethoxy group), and a triplet at 1.12 ppm (J_{HH} = 7 Hz, methyl hydrogens of the ethoxy group). The ring methylene hydrogens are found at δ 2.68 (J_{PH} = 11 Hz). At 75° the spectrum is unchanged except that the absorption due to the methylene hydrogens of the ethoxy groups is now broad and ill defined; at 50° it has sharpened into a many-line pattern. The low-temperature spectra are readily understandable in terms of the pseudorotation processes discussed for **1**.

The apparent equivalence of the methylene hydrogens of the ethoxy groups of **2** at 100° can arise if structures containing a diequatorial ring are permitted. If the Berry mechanism for pseudorotation is assumed,[4a] then a minimum of five pseudorotations in which each group bonded to phosphorus is used as a pivot leads to isochronous hydrogens of the methylene groups. Apparent equivalency can arise as discussed above; however, coalescence is not predicted.

Previous work with four-membered-ring phosphoranes in which an oxygen is bonded to phosphorus in the ring has shown that these substances do not pseudorotate rapidly on the nmr time scale.[6] On the other hand, pseudorotation has been implicated in various reactions of four-membered-ring phosphorus-containing compounds.[4e] No experimental evidence has been presented for a diequatorial ring, although it has been suggested.[7] Later work has shown that a diequatorial ring is not required to explain the results.[8] Calculations have attested to the possibility of such a geometry.[4e]

(6) (a) F. Ramirez, C. P. Smith, and J. F. Pilot, *J. Amer. Chem. Soc.*, **90**, 6726 (1968); (b) F. Ramirez, C. P. Smith, J. F. Pilot, and A. S. Gulati, *J. Org. Chem.*, **33**, 3787 (1968).

(7) P. Haake, R. D. Cook, T. Koizumi, P. S. Ossip, W. Schwartz, and D. A. Tyssee, *J. Amer. Chem. Soc.*, **92**, 3828 (1970).

(8) J. R. Corfield, N. J. De'Ath, and S. Trippett, *Chem. Commun.*, 1502 (1970).

(9) National Institutes of Health Postdoctoral Fellow, 1969–1970, Grant No. GM-43655.

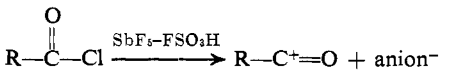
Dorothy Z. Denney, Dennis W. White,[9] Donald B. Denney*
Department of Chemistry, Rutgers University
New Brunswick, New Jersey 08903
Received November 23, 1970

Reversal of a Substituent Effect on Cation Stabilities between the Gas and Liquid Phases

Sir:

In spite of the enormous amount of work done on substituent effects in organic chemistry, studies in which gas-phase and solution data can be compared are rare.[1–5] We wish to report such a comparison for the formation of substituted oxocarbonium ions (R—C$^+$=O) in the gas phase and in "magic acid" solution. A normal inductive order is observed in the gas phase while a Baker–Nathan order is observed in solution.

Using the techniques developed by Arnett and Larsen[6] the relative heats of formation of several oxocarbonium ions from the corresponding acid chlorides were measured calorimetrically in 11.5 mol % antimony pentafluoride in fluorosulfonic acid at 25°. The reaction is shown in eq 1 and the data are given in



$$\mathrm{R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}Cl} \xrightarrow{\mathrm{SbF_5{-}FSO_3H}} \mathrm{R{-}C^{+}{=}O} + \text{anion}^- \qquad (1)$$

Table I. The oxocarbonium ions are well known in strong acids[7] and, except for the ion from pivoyl chloride, are stable in this solvent at 25° as verified by nmr studies. The *tert*-butyloxocarbonium ion decarbonylates at room temperature.[8] It is stable at −60°, however, and the value reported in Table I was measured at this temperature. The heats of formation of the methyl- and cyclopropyloxocarbonium ions were the same at 25 and −60°, so the errors introduced by this extrapolation are small.[9] It is obvious from the data in Table I that a large Baker–Nathan order exists. Also shown in Table I are the heats of solution of the acid chlorides in nitromethane. It has recently been shown[10] that Baker–Nathan orders can be generated by cavity effects on transferring a series of solutes from one solvent to a second solvent of higher cohesive energy density. This effect is indeed observed here, but it is too small to explain the observed Baker–Nathan order.

Table I. Relative Heats of Formation (ΔH_{R^+}) of Acylium Ions in 11.5 mol % SbF_5–FSO_3H at 25°

R	$\Delta\bar{H}_{\mathrm{S,CCl_4}}$, kcal/mol	ΔH_{R^+}, kcal/mol	$\Delta\bar{H}_{\mathrm{S,CH_3NO_2}}$
Me	+0.96 ± 0.01	−21.2 ± 0.2	+0.25 ± 0.02
Et	+0.83 ± 0.03	−19.4 ± 0.3	+0.58 ± 0.01
i-Pr	+0.47 ± 0.01	−19.0 ± 0.3	+1.01 ± 0.05
tert-Bu	+0.46 ± 0.02	−16.1 ± 1.2	+1.25 ± 0.02

The heats of formation for the methyl-, ethyl-, and isopropyloxocarbonium ions in the series are known in the gas phase.[11] We have selected the data of Murad and Inghram[12] to give a very reliable set of data from the same source. These are presented in column 1 of Table II. To obtain the heat of formation for the *tert*-butyloxocarbonium ion, semiempirical calculations using the MINDO approximation[13,14] were

(1) J. I. Brauman and L. K. Blair, *J. Amer. Chem. Soc.*, **92**, 5986 (1970); **90**, 6561 (1968).

(2) J. L. Franklin, *Trans. Faraday Soc.*, 48, 443 (1952).

(3) A. Maccoll, *Advan. Phys. Org. Chem.*, 3, 91 (1965); *Chem. Rev.*, **69**, 33 (1969).

(4) J. L. Franklin, "Carbonium Ions," Vol. 1, G. A. Olah and P. v. R. Schleyer, Ed., Wiley, New York, N. Y., 1968.

(5) W. M. Schubert, R. B. Murphy, and J. Robins, *J. Org. Chem.*, **35**, 951 (1970), and references therein.

(6) E. M. Arnett and J. W. Larsen in ref 4, p 441.

(7) H. Hogeveen and C. J. Gaasbeek, *Recl. Trav. Chim. Pays-Bas*, **89**, 395 (1970); H. Hogeveen, F. Baardman, and C. F. Roobeek, *ibid.*, **89**, 227 (1970); R. C. Paul, R. D. Sharma, and K. C. Malhotra, *Can. J. Chem.*, 48, 2124 (1970); G. A. Olah and A. M. White, *J. Amer. Chem. Soc.*, **91**, 5801 (1969); D. A. Tomalia, *J. Org. Chem.*, 34, 2583 (1969); H. Hogeveen, J. Lukas, and C. F. Roobeek, *Chem. Commun.*, 920 (1969); G. A. Olah and M. B. Comisarow, *J. Amer. Chem. Soc.*, **88**, 3313 (1966); N. C. Deno, C. U. Pittman, Jr., and M. J. Wisotsky, *ibid.*, **86**, 4370 (1964); G. A. Olah, W. S. Tolgyesi, S. J. Kuhn, M. E. Moffatt, I. J. Bastien, and E. B. Baker, *J. Amer. Chem. Soc.*, **85**, 1328 (1963).

(8) There has been a recent nmr study of the equilibration of secondary and tertiary carbonium ions with their oxocarbonium ions which includes some data on the free energy of difference between substituted oxocarbonium ions: H. Hogeveen and C. F. Roobeek, *Recl. Trav. Chim. Pays-Bas*, **89**, 1211 (1970).

(9) This technique also yields the heats of decarbonylation of the oxocarbonium ions. Studies of this process are in progress and will be the subject of a full paper.

(10) J. W. Larsen, P. A. Bouis, and D. B. Glass, Jr., submitted for publication.

(11) 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 Positive Ions," National Bureau of Standards Publication No. NSRDS-NBS-26, U. S. Government Printing Office, Washington, D. C., 1969.

(12) E. Murad and M. C. Inghram, *J. Chem. Phys.*, 40, 3263 (1964).

Table II. Heats of Formation of the Acylium Ions (R—C$^+$=O) in the Gas Phase

R	ΔH_f, kcal/mol Exptl[a]	ΔH_f, kcal/mol Calcd[b]
Me	153	157
Et	143	145
i-Pr	133	133
tert-Bu		121

[a] Reference 11. [b] Calculated using the MINDO approximations.

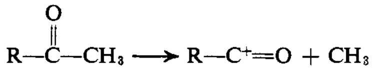
carried out. The results of these calculations are shown in column 2 of Table II. The C–O and C–C$^+$ bond lengths were taken from the literature[15] and the remaining C–C and C–H bond lengths are shown in Table III. All parameters for the one-electron resonance integrals were the same as given by Baird[14] except for β_{CO}^{II}, which was changed to 0.032 to adjust for the short C—O bond distance in R—C$^+$=O.

Table III. Geometries Used in MINDO Calculations of Heats of Formation of the Oxocarbonium Ions

Bond	Length, Å	Bond	Angle, deg
C$^+$–O	1.108[a]	C–C$^+$–O	180
C–C$^+$	1.385[a]	$^+$C–C–H	108
C–H (α-C)	1.070	$^+$C–C–C	108
C–C	1.500		
C–H (methyl)	1.100 ± 0.005		

[a] Reference 15.

It would be nice to compare heats of formation of the ions in the gas and liquid phases, but the necessary thermochemical data on the acid chlorides are unavailable. The requisite measurements are currently underway here. However, the substituent effects on heats of reaction to give the cation in the gas phase and in solution are readily available. The gas-phase heats of formation from Table II can be combined with the gas-phase heats of formation of the methyl ketones and CH$_3$ to give the heats of reaction 2 in



$$R\text{—}\overset{\displaystyle O}{\overset{\|}{C}}\text{—}CH_3 \longrightarrow R\text{—}C^+\text{=}O + CH_3 \qquad (2)$$

the gas phase. These data are shown in Table IV. Since we are interested in substituent effects, the leaving-group effects will cancel in each series. Thus the heats of reaction in Tables I and IV show the effect of changing substituents on the difference in energy between the starting material and ionic product.

Table IV. Heats of Reaction 2 in the Gas Phase at 25°

R	ΔH_R, kcal/mol
Me	+238
Et	+234
i-Pr	+229
tert-Bu	+225[a]

[a] Calculated using the heat of formation of *tert*-Bu—C$^+$=O given in Table II (MINDO) and the heats of formation of *tert*-butyl methyl ketone and CH$_3$ from ref 11. A slightly lower value (223 kcal/mol) is obtained if the heat of formation of methyl *tert*-butyl ketone reported by Cox and Pilcher is used: J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds," Academic Press, New York, N. Y., 1970, p 208.

The data in Tables I and IV permit a direct comparison between the substituent effect on a reaction in the gas phase and in solution.[16] The normal inductive order which is observed in the gas phase becomes a Baker–Nathan order in solution. This is a case where the Baker–Nathan order must be ascribed to solvent effects.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work. Partial support by the National Science Foundation is also gratefully acknowledged.

---

(13) N. C. Baird and M. J. S. Dewar, *J. Chem. Phys.*, **50**, 1262 (1969).

(14) N. C. Baird, M. J. S. Dewar, and R. Sustmann, *ibid.*, **50**, 1275 (1969).

(15) F. P. Boer, *J. Amer. Chem. Soc.*, **90**, 6706 (1968).

(16) For the most recent in a long series of papers reporting investigations of the difference in the substituent effect of simple alkyl groups in the gas phase and in solution, see ref 5. Schubert's work contains several examples of substituent effects on electronic transitions which are reversed on passage from the gas phase to a solvent.

John W. Larsen,* Paul A. Bouis
Michael W. Grant, Charles A. Lane
Department of Chemistry, University of Tennessee
Knoxville, Tennessee 37916

January 19, 1971

Appropriate Nonbonding Orbitals for Describing Photophysical Properties in Benzaldehyde[1]

Sir:

Early valence views conceived of a lone-pair electron density highly concentrated at the carbonyl oxygen.[2] More recently a number of all-valence-electron calculations yielded very substantial delocalization of all valence orbitals in the ground state.[3] Admittedly, these calculations are as yet inexact; nevertheless, no support to the localized or delocalized view can be given by MO theory because the distinction between "localized" and "nonlocalized" orbitals is not an unambiguous one. It is possible to localize or delocalize an orbital at will by suitable unitary transformations among the occupied orbitals with no change in the total wave function for a given state. Any ground-state observable must then be predicted equally well by localized or delocalized orbitals.

In describing an excited state, a construct primarily used is the virtual-orbital model.[4] In this model, the excited-state wave function (Ψ_S) is obtained from the ground state (Ψ_0) by replacing one (or more) of the ground-state orbitals by virtual orbitals. An important feature of this construct is that orbitals common to both states are not reorganized. Not all unitary transformations on the occupied ground-state orbitals will leave such an excited-state wave function unaffected, so that observables computed with the excited-state wave function will in general be dependent on the transformation.

---

(1) (a) Supported by National Science Foundation Grant No. GP 6301X; (b) presented at the EUCHEM Conference on Photophysical Processes, Schloss Elmau, Germany, Oct 25–31, 1970.

(2) R. S. Mulliken, *J. Chem. Phys.*, **3**, 564 (1935).

(3) *E.g.*, (a) J. M. Hollas, E. Gregorek, and L. Goodman, *ibid.*, **49**, 1745 (1968); (b) D. B. Neumann and J. W. Moskowitz, *ibid.*, **50**, 2216 (1969); (c) R. Hoffmann and J. R. Swenson, *J. Phys. Chem.*, **74**, 415 (1970); (d) E. Clementi, *J. Chem. Phys.*, **46**, 4737 (1967), for azines.

(4) *E.g.*, R. S. Mulliken, *J. Chim. Phys., Physicochim. Biol.*, **46**, 497 (1949); C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951).