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References and Notes

(1) E. Gil-Av and J. Herling, *J. Phys. Chem.*, **66**, 1208 (1962).
(2) M. A. Muhs and F. T. Weiss, *J. Am. Chem. Soc.*, **84**, 4697 (1962).
(3) R. J. Cvetanovic, F. J. Duncan, and W. E. Falconer, *Can. J. Chem.*, **42**, 2410 (1964).
(4) J. H. Purnell, "Gas Chromatography", A. B. Littlewood, Ed., The Institute of Petroleum, London, 1966, p 3.
(5) H. L. Liao, D. E. Martire, and J. P. Sheridan, *Anal. Chem.*, **45**, 2087 (1973).
(6) G. M. Janini and D. E. Martire, *J. Phys. Chem.*, **78**, 1644 (1974).
(7) C. Eon, C. Pommier, and G. Guichon, *J. Phys. Chem.*, **75**, 2632 (1971).
(8) C. Eon and B. Karger, *J. Chromatogr. Sci.*, **10**, 140 (1972).
(9) D. L. Meen, F. Morris, and J. H. Purnell, *J. Chromatogr. Sci.*, **9**, 281 (1971).
(10) O. P. Srivastava and J. H. Purnell, *Anal. Chem.*, **45**, 1111 (1973).
(11) C. Eon, C. Pommier, and G. Guichon, *C. R. Hebd. Seances Acad. Sci.*, **168**, 1553 (1969).
(12) C. Eon and G. Guichon, *Anal. Chem.*, **46**, 1393 (1974).
(13) D. F. Cadogan and J. H. Purnell, *J. Chem. Soc.*, 2133 (1968).
(14) A.P.I. Research Project 44, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds", Carnegie Press, Pittsburgh, Pa., 1953.
(15) D. E. Martire and P. Riedl, *J. Phys. Chem.*, **72**, 3478 (1968).
(16) H. L. Liao and D. E. Martire, *J. Am. Chem. Soc.*, **96**, 2058 (1974).
(17) J. P. Sheridan, D. E. Martire, and Y. B. Tewari, *J. Am. Chem. Soc.*, **94**, 3294 (1972).
(18) J. P. Sheridan, D. E. Martire, and F. P. Banda, *J. Am. Chem. Soc.*, **95**, 4788 (1973).
(19) D. L. Meen, F. Morris, J. H. Purnell, and O. P. Srivastava, *J. Chem. Soc., Faraday Trans. 1*, **69**, 2080 (1973).

Solution and Complexing Studies. II. Comparison and Correlation of Nuclear Magnetic Resonance and Gas–Liquid Chromatographic Data

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Abstract: An NMR study of the effects of adding chloroform, 1,2-dichloroethane, benzene, toluene, ethylbenzene, *o*-xylene, *m*-xylene, or *p*-xylene to both di-*n*-octyl ether (DNOE)/*n*-heptadecane and di-*n*-butyl tetrachlorophthalate (DNBT)/squalane mixtures at 30° has been carried out. Both solvent systems are miscible over the whole concentration range. Conventionally evaluated complexing stability constants (equilibrium quotients) are shown to be relatively inconsistent and to correlate poorly with corresponding GLC based data. A model based on partitioning of the volatile electron donors between notionally immiscible electron acceptor and inert solvent mixture components leads to an equation relating chemical shifts with the relevant partition coefficients. This, in turn, leads to an equation connecting chemical shifts with GLC determined partition coefficients which provides a remarkable correlation of the data. This correlation provides a means to predict chemical shifts quantitatively from solution data. The evidence raises serious questions as to the meaning of NMR evaluated stability constants and indicates a need to reconsider theories of both nonelectrolyte solutions and of weak molecular complexes.

The measurement of stability (formation) constants, or more correctly equilibrium quotients, of chemical complexes by the NMR method is now well established and widespread. In essence, the method consists in measuring chemical shifts as a function of concentration of one or the other of the reactants A and D in an inert solvent S. If, for arguments sake, we consider the situation wherein the concentration of D in S is held constant then, for a 1:1 complex, the stability constant (K_1) for formation of AD is related to the chemical shifts via

$$1/\Delta = (1/K_1\Delta^0 C_A) + (1/\Delta^0) \qquad (1)$$

where Δ^0 is the chemical shift difference ($\delta_S{}^0 - \delta_{AD}$), Δ is the difference ($\delta^0{}_S - \delta$) where δ is the measured shift, and C_A is the molar concentration of A. This equation is formally identical with the Benesi-Hildebrand equation which is used to process conventional spectroscopic data and, like the latter, may be reorganized into one or another of several forms for the purpose of graphical or numerical evaluation of K_1 from the data.

Several studies of weak molecular complexing involving concurrent use of both GLC and spectroscopic methods have been reported.[1-4] Only rarely have the quantitative data agreed even approximately and there are numerous examples of negative values of K_1 derived from the spectroscopic data; in general, GLC and NMR data are in serious conflict and there is only poor correlation between NMR and uv-visible data as well. On account of this we have elsewhere[2] suggested that GLC data are, on the whole, more likely to be reliable but that this, in itself, does not establish the validity even of these data. The findings with respect to GLC measured values of K_1 reported in part I[5] must add further to our concern regarding the above discrepancies. We have, thus, undertaken an NMR study of most of the GLC systems discussed in part I.

Experimental Section

Measurements were made with a Varian HA100D spectrometer operating at 100 MHz for ^{1}H. Sweep width calibration was carried out with a signal generator and a Varian V4315 frequency counter. The variable temperature controller was calibrated by following the separation of the two major peaks of the glycol spectrum.

Chemical shifts were measured via the reciprocals in order to improve precision. Water-free acetone was used as an external reference.

Results

Data were processed, via least-squares computer programs, to evaluate K_1 via eq 1 and its commonly preferred alternative formulations due to Scott[6] and Foster.[7] The latter two procedures yielded essentially the same result in most instances but a substantial difference from this was commonly noted in the value derived via eq 1. The reasons for this have been discussed on many occasions and need no repetition.

Table I. Computed Least-Squares Values of K_1 (l. mol^{-1}) from NMR Data

A. Di-*n*-octyl Ether (A) in Heptadecane (S) at 30° with Named Reactants (D)[a]			
$CHCl_3$	0.305	1,2-$C_2H_4Cl_2$	0.036
B. Di-*n*-butyl Tetrachlorophthalate (A) in Squalane (S) at 30° with Named Reactants (D)			
$CHCl_3$	0.590	Ethylbenzene	0.465
1,2-$C_2H_4Cl_2$	0.131	*o*-Xylene	0.510
Benzene	0.476	*m*-Xylene	0.345
Toluene	0.520	*p*-Xylene	0.545

[a] No measureable shifts with aromatic reactants (D).

Figure 1 illustrates a selection of plots of data according to eq 1 which, despite its shortcomings, is the most familiar method. The lines drawn correspond to the computed data and the data are clearly adequately linear. The plots illustrated are typical of those pertaining to all the systems studied. Further, equally acceptable plots of the data in terms of both mole fraction and volume fraction of A were obtained. The several types of K_1 evaluated in terms of the different concentration units were precisely connected by the equations connecting K_1 in the three sets of units[2,8,9] irrespective of whether eq 1 or its variants were used or whether or not the differently derived values of K_1 agreed.

Table I lists the results obtained. No measureable chemical shifts were observed with the systems of aromatics/DNOE/heptadecane; the corresponding GLC values were essentially consistent with this in that they ranged only in the range of trivial values between 0.03 and 0.09 l. mol^{-1}. In contrast, GLC yielded the value 0.235 l. mol^{-1} for 1,2-dichloroethane, a result much removed from the NMR result, and the very discrepant value of 0.407 l. mol^{-1} for chloroform. Thus, where there was anything to measure, agreement was poor. For the reactions involving DNBT/squalane solutions there is reasonable (±25%) agreement between the GLC and NMR data except, once more, for 1,2-dichloroethane, where the GLC value is 0.745 l. mol^{-1}. In general, therefore, the extent of agreement is rather better than has been noted by us before but is still, on the whole, rather poor. Further, there are clear inconsistencies in the relative NMR values of K_1 for the various aromatics. It may be suggested that corrections for variation in bulk magnetic susceptibility, since an external reference was used, would alter the situation. In fact, the recommended procedure[10] led to more than one-third of the NMR evaluated K_1 becoming negative. Since also, as we show later, the uncorrected data can be correlated with the GLC data on a different basis, we are forced to conclude that the recommended correction is valueless in this instance.

In summary, therefore, the present analysis based on conventional lines is no more informative than has been indicated by previous studies.

Discussion

The observation described[5] in part I that all GLC data for nominally complexing systems can be described by the solution equation

$$K_R = \phi_A K_{R(A)}{}^0 + \phi_S K_{R(S)}{}^0 \qquad (2)$$

and that the results are compatible with a model which, in the most simple terms, allows A and S to be regarded as immiscible, suggests that a similar view applied to the NMR data might permit a new insight and a correlation of the GLC and NMR results.

Where there is rapid transfer of a proton between two environments the simplest definition of the observed chemical shift, δ, is

$$\delta = \Sigma P_i \delta_i$$

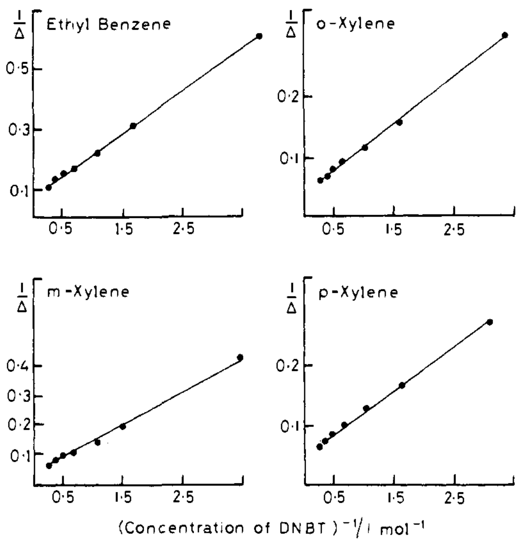

Figure 1. Illustration of applicability of conventional, Benesi–Hildebrand type equation to NMR data for representative systems. Solvent, DNBT/squalane at 30°.

where P_i is the fractional population of the nucleus in the ith environment and δ_i is the shift which would be observed in that environment. If, thus, we assume A and S to be immiscible, but transfer of D between them to be rapid,

$$\delta = P_A \delta_A{}^0 + P_S \delta_S{}^0$$

where the zero superscript designates the shift in a pure liquid. Hence, since

$$P_A + P_S = 1$$

it follows that

$$P_A = (\delta - \delta_S{}^0)/(\delta_A{}^0 - \delta_S{}^0) = \Delta/\Delta^0 \qquad (3)$$

Alternatively, we may define

$$P_A = n_{DA}/[n_{DA} + n_{DS}]$$

where n_D symbolizes the number of moles of reactant D in a given solvent. Dividing top and bottom by $(V_A + V_S)$, the total solvent volume, and recalling that

$$(V_A + V_S)^{-1} = \phi_A/V_A = \phi_S/V_S$$

we have

$$P_A = [\phi_A n_{DA}/V_A/(\phi_A n_{DA}/V_A) + (\phi_S n_{DS}/V_S)]$$

Dividing top and bottom by n_{Dg} where the subscript defines the gas phase appropriate to the system, and recognizing that

$$[n_{DA}/V_A]/[n_{Dg}/V_g] = K_{R(A)}{}^0$$

and

$$[n_{DS}/V_S]/[n_{Dg}/V_g] = K_{R(S)}{}^0$$

where $K_R{}^0$ is a liquid/gas partition coefficient[5] for D, we get

$$P_A = \Delta/\Delta^0 = \phi_A K_{R(A)}{}^0/[\phi_A K_{R(A)}{}^0 + \phi_S K_{R(S)}{}^0] \qquad (4)$$

This is, therefore, the basic NMR equation for a three-component partitioning system.

We showed[5] in part I that, for the systems under study here, the denominator in eq 4 is equal to the "overall" liquid/gas partition coefficient, K_R, hence, eq 4 becomes

$$\Delta/\Delta^0 = \phi_A K_{R(A)}{}^0/K_R \qquad (5)$$

an equation relating the NMR (lhs) and GLC (rhs) data

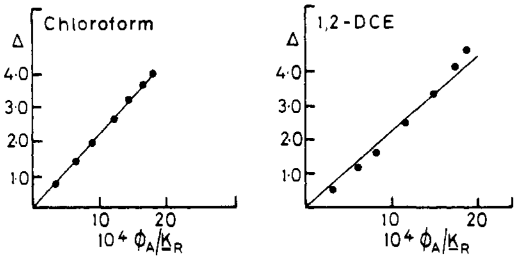

Figure 2. Plots of Δ (ppm) against ϕ_A/K_R for named compounds in DNOE/*n*-heptadecane mixtures at 30°.

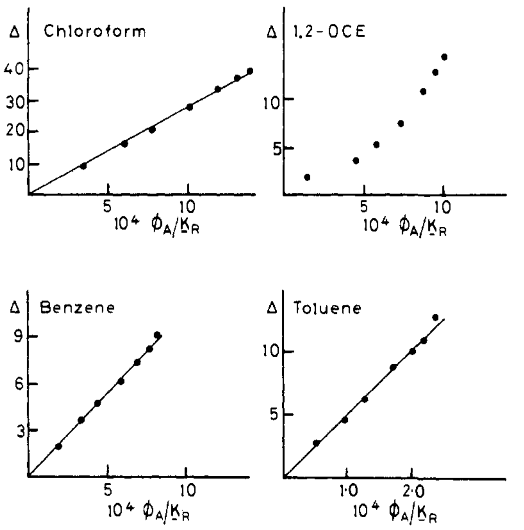

Figure 3. Plots of Δ (ppm) against ϕ_A/K_R for named compounds in DNBT/squalane mixtures at 30°.

for the same value of C_A explicitly. We may thus test our model by plotting Δ against ϕ_A/K_R, the latter data deriving from part I of this work.[5] Such plots are illustrated in Figures 2-4. The lines drawn represent the computed least-squares lines and are seen to represent the data well and to have zero or trivial intercepts, except in the single case of 1,2-dichloroethane/DNBT/squalane at high ϕ_A. Table II lists both the computer calculated slopes of these plots and those calculated separately from the product $(K_{R(A)}{}^0\Delta^0)$. The agreement is quite remarkable and totally confirms both the quality of the data and the validity of the model. Even the data for 1,2-dichloroethane/DNBT/squalane at low ϕ_A show excellent conformity. So far as is known to us, this is the first real correlation of NMR and GLC data for systems supposed to exhibit chemical complexing. It may be argued that the conventional complexing equations, (1) and[5]

$$K_R = K_{R(S)}{}^0\,(1 + K_1C_A) \qquad (6)$$

would lead to a similar result. Equating the product K_1C_A from eq 1 and 6 leads, after rearrangement, to

$$\Delta = \Delta^0 - [K_{R(S)}{}^0\Delta^0/K_R] \qquad (7)$$

which is to be compared with eq 5. We see that this equation (a) predicts a negative slope of the plot of Δ against $K_R{}^{-1}$ and (b) contains no term in ϕ_A. Not surprisingly, in the light of what has been shown earlier, all plots of our data according to this method were strongly curved and, furthermore, curved positively.

A final possibility to be considered is that, for fundamental reasons, the K_1 of eq 1 and 6 are not equatable. On this view, one or the other or both would have to be assumed to be incorrect or incorrectly identified. We recognize this possibility since we have shown earlier that evaluation of the data via the two equations provides results in poor accord. It is possible, for instance, that as has been suggested by Martire,[11] $K_1{}^{GLC}$ contains additive contributions from the K_1 of the charge-transfer or other complexing and the K_1 arising from collision pairing whereas $K_1{}^{NMR}$ comprises only the former. However, introducing this into our theory we would still derive an equation similar to (7), which we know does not fit. In contrast, the immiscibility model provides quantitative compatibility of the data. We cannot ignore the evidence and so must assume either that these systems exhibit no complexing (in the usual definition of this phenomenon) or as is much more likely that, if they do, it cannot be mathematically described in conventional terms associated hitherto with totally random distribution of reactants in solvent.

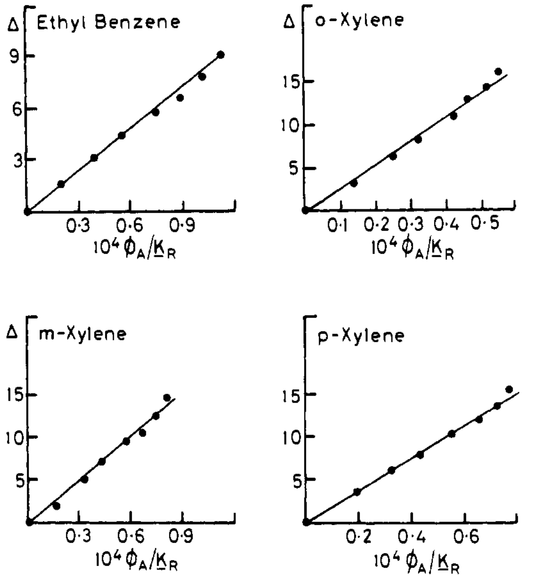

Figure 4. Plots of Δ (ppm) against ϕ_A/K_R for named compounds in DNBT/squalane mixtures at 30°.

Table II. Comparison of Slopes of Plots According to Equation 5 and Calculated Values

	DNOE/heptadecane		DNBT/squalane	
	Slope	$K_{R(A)}{}^0\Delta^0$	Slope	$K_{R(A)}{}^0\Delta^0$
$CHCl_3$	23,176	23,182	28,427	28,424
1,2-$C_2H_4Cl_2$	2,490	2,495	14,358	14,465
Benzene			11,090	10,890
Toluene			52,887	51,400
Ethylbenzene			81,016	77,356
o-Xylene			288,939	285,490
m-Xylene			175,365	173,002
p-Xylene			199,240	191,945

This NMR investigation provides confirmation of our solution study and further indicates the immediate need to reevaluate current thinking about both solution and weak complexing theory. Further, it is clear that the large volume of spectroscopically determined stability constants now to be found in the literature must be viewed with considerable suspicion. We propose to discuss this matter in greater detail in a subsequent article.

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References and Notes

(1) D. L. Meen, F. Morris, and J. H. Purnell, *J. Chromatogr. Sci.*, **9**, 281 (1971).
(2) J. H. Purnell and O. P. Srivastava, *Anal. Chem.*, **45**, 1111 (1973).
(3) C. Eon, C. Pommier, and G. Guichon, *C. R. Hebd. Seances Acad. Sci.*,

168, 1553 (1969).
(4) C. Eon and G. Guichon, *Anal. Chem.*, **46**, 1393 (1974).
(5) J. H. Purnell and J. M. Vargas de Andrade, preceding paper in this issue.
(6) R. L. Scott, *Recl. Trav. Chim. Pay-Bas*, **75**, 787 (1956).
(7) R. Foster, D. Ll. Hammick, and A. A. Wardley, *J. Chem. Soc.*, 3817 (1953).
(8) I. D. Kuntz, F. P. Gasparro, M. D. Johnston, and R. P. Taylor, *J. Am. Chem. Soc.*, **90**, 4778 (1968).
(9) J. Homer, M. H. Everdell, C. J. Jackson, and P. M. Whitney, *J. Chem. Soc. Faraday Trans. 2*, **68**, 874 (1972).
(10) K. Feri and H. J. Bernstein, *J. Chem. Phys.*, **37**, 1891 (1962).
(11) D. E. Martire, *Anal. Chem.*, **46**, 1712 (1974).

Crossed Beam Isotope Labeled Studies of Short-Lived Reaction Intermediates. $CH_3^+ + C_2H_4$

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Abstract: Crossed beam studies of the ion-molecule reaction $CH_3^+ + C_2H_4 \rightarrow C_2H_3^+ + C_2H_3$ and related isotopic variants involving deuterated and ^{13}C labeled reactants indicate that all products are formed by a direct mechanism, as opposed to a long-lived complex. The ionic products are scattered forward over an energy range of 0.7 to 3.0 eV (CM), with only minor kinematic differences among the various isotopic species. A kinetic model of scrambling and dissociation in a near linear intermediate accounts for the observed relative cross sections of the isotopic products. There is some indication protonated cyclopropane intermediates may play a role at lower energies.

I. Introduction

Carbonium ions represent an important group of reaction intermediates. Our studies of carbonium ion reactions, using beam techniques, provide information on the structure and rearrangements of these ions. Rearrangement in such ions has been studied by NMR and by unimolecular decomposition in mass spectrometers. Two recent reviews are available.[1,2] In addition, some studies of hydrocarbon ion-molecule reactions, involving such intermediates, have been undertaken. These investigations have examined reaction dynamics[3] or isotopic scrambling[4,5] and have focused either on the kinematics of reactive collisions or on the structures of the intermediate species. Our experiments combine these two kinds of information[6] over a range of reaction energies to check the consistency of these two approaches to chemical reactivity and to increase our knowledge of the behavior of this important category of ion-molecule reaction. We report here work on the reaction

$$CH_3^+ + C_2H_4 \longrightarrow C_2H_3 + CH_4 \qquad (1)$$

Extensive research and debate has centered on the structures of $C_3H_7^+$, the intermediate ion in this reaction. Some possible structures for this ion, including a cyclic structure, are shown in Figure 1, with heats of formation given in Table I. Theoretical values are from CNDO calculations of Pople et al.[7]

Using the crossed beam apparatus EVA,[8] we have studied the following variants of reaction 1 at relative (CM) collisional energies from 0.7 to 3.0 eV:

$$^{13}CH_3^+ + C_2H_4 \longrightarrow C_2H_3^+(\text{mass } 27) + {}^{13}CH_4 \qquad (2a)$$

$$\longrightarrow {}^{13}CCH_3^+(28) + CH_4 \qquad (2b)$$

$$CH_3^+ + C_2D_4 \longrightarrow C_2H_3^+(27) + CD_4 \qquad (3a)$$

$$\longrightarrow C_2H_2D^+(28) + CD_3H \qquad (3b)$$

$$\longrightarrow C_2HD_2^+(29) + CD_2H_2 \qquad (3c)$$

$$\longrightarrow C_2D_3^+(30) + CDH_3 \qquad (3d)$$

By measuring the mass, angle, and energy distributions of the products, we have obtained probability contour plots in velocity space indicating the kinematics of the reactions above. In additions, relative cross sections for the different products were calculated[6] at each energy studied.

It is our purpose in this study to determine the extent and pattern of isotopic scrambling in reactions 2 and 3 at various energies; the extent of kinematic differences between different isotopic products; what model or models, if any, involving the intermediate structures in Figure 1 predict the observed isotopic scrambling; and whether the scrambling model is consistent with the kinematics. The model should involve some intramolecular hydrogen migration process for scrambling, in competition with the dissociation of the reaction intermediate to products.

Other experimental work has utilized various $C_3H_7^+$ sources and observed the extent of isotopic scrambling over a wide range of energies and time scales. Saunders et al.[1] have observed scrambling of H and ^{13}C atoms in solutions of isopropyl cation by NMR techniques at 0-40°. They have proposed several possible mechanisms to explain the data including a process required for carbon scrambling involving protonated cyclopropane. Lias, Rebbert, and Ausloos[9] have observed geometrical and isotopic scrambling in $C_3H_7^+$ produced by the radiolysis of *n*-butane and isobutane. The ion cyclotron resonance of McAdoo et al.[10] shows nearly complete hydrogen scrambling in metastable *n*- and *sec*-$C_3H_7^+$ ions produced by electron impact. Nondecomposing *n*-$C_3H_7^+$ ions of lower energy isomerized to *sec*-$C_3H_7^+$, but showed little additional hydrogen scrambling on the ICR time scale ($\sim 10^{-3}$ sec). The present work concerns $C_3H_7^+$ produced by chemical reaction at higher energies and shorter lifetimes than in the previous results.

II. Experimental Section

The apparatus EVA is described in detail elsewhere.[8] Two beam sources are mounted at 90° from each other on a rotatable lid. As the lid is rotated, a detection system scans the angular distributions of products. The ion beam is produced by electron bombardment, mass selected by acceleration into a small permanent magnet, and focused and decelerated to the desired energy by a series of electro-

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