[a] Only cases of rate-determining addition are considered since in other situations differentiations between the two mechanisms are easily achieved by kinetics alone. [b] Dependent on the concentrations and the nature of the alkene. [c] Becomes faster on increasing the acidity of the solvent. [d] Rate enhancement is expected in the case of electrophilic assistance by the formed proton *via* protonation of the leaving group. [e] Except for solvation or special interactions with the leaving group. [f] Except for salt effects. [g] Addition by the solvent. [h] Especially for protonation on the α carbon provided that the $^+CR_2R_3$ ion is more stable than the $^+CR_1X$ ion. [i] In the absence of neighboring group participation. The actual direction of the change depends on the balance of the inductive and the conjugative effects. [j] Although not necessarily observable. [k] Depending on the relative rates of protonation, ionization, internal rotation, and product formation. [l] The steric effects determining the *cis–trans* ratios of the products are expected to be similar in the transition states of both routes. [m] For S = H. [n] For R_3 = H. [o] A concerted elimination cannot be excluded. [p] C. A. Grob and G. Cseh, *Helv. Chim. Acta*, **47,** 194 (1964). [q] Z. Rappoport and A. Gal, *J. Amer. Chem. Soc.*, **91,** 5246 (1969). [r] C. A. Grob and R. Spaar, *Tetrahedron Lett.*, 1439 (1969). [s] P. J. Stang and R. H. Summerville, *J. Amer. Chem. Soc.*, **91,** 4600 (1969). [t] Z. Rappoport and Y. Apeloig, *ibid.*, **91,** 6734 (1969). [u] P. E. Peterson and J. M. Indelicato, *ibid.*, **91,** 6194 (1969). [v] S. A. Sherrod and R. G. Bergman, *ibid.*, **91,** 2115 (1969). [w] M. Hanack and T. Bässler, *ibid.*, **91,** 2117 (1969). [x] L. L. Miller and D. A. Kaufman, *ibid.*, **90,** 7282 (1968). [y] Z. Rappoport and Y. Kaspi, *ibid.*, **92,** 3220 (1970). [z] W. M. Jones and D. D. Maness, *ibid.*, **91,** 4314 (1969). [aa] Z. Rappoport and A. Gal, submitted for publication. [bb] D. R. Kelsey and R. G. Bergman, *J. Amer. Chem. Soc.*, **92,** 228 (1970). [cc] G. Capozzi, G. Melloni, G. Modena, and M. Piscitelli, *Tetrahedron Lett.*, 4039 (1968). [dd] M. D. Schiavelli, S. C. Hixon, and H. W. Moran, *J. Amer. Chem. Soc.*, **92,** 1082 (1970). [ee] G. Modena and U. Tonellato, *Chem. Commun.*, in press. [ff] Z. Rappoport and Y. Apeloig, submitted for publication. [gg] Z. Rappoport and Y. Apeloig, *Israel J. Chem.*, **7,** 34p (1969). [hh] Z. Rappoport, Y. Kaspi, and Y. Apeloig, unpublished results. [ii] Reference 1. [jj] Z. Rappoport and A. Gal, unpublished results. [kk] S. J. Huang and M. V. Lessard, *J. Amer. Chem. Soc.*, **90,** 2432 (1968). [ll] G. Modena, U. Tonellato, and F. Naso, *Chem. Commun.*, 1363 (1968). [mm] G. Modena and U. Tonellato, *ibid.* 1676 (1968). [nn] G. Capozzi, G. Melloni, G. Modena, and U. Tonellato, *ibid.*, 1520 (1969). [oo] P. E. Peterson and J. M. Indelicato, *J. Amer. Chem. Soc.*, **90,** 6515 (1968). [pp] M. A. Imhoff, R. H. Summerville, P. v. R. Schleyer, A. G. Martinez, M. Hanack, T. E. Dueber, and P. J. Stang, *ibid.*, **92,** 3802 (1970). [qq] R. G. Berman, unpublished results.

An additional argument for route A is the rearrangement of vinyl derivatives in solvolysis reactions. It is difficult to explain the products without suggesting vinyl cation intermediates. Examples are the solvolysis of *t*-butylvinyl triflate,[7] and 1-adamantylvinyl triflate,[8] leading predominantly to rearranged products, and the solvolysis of **9**[9] and **11**.[8] Additional examples for rearrangement reactions involving vinyl cations will be published in the near future.[10]

In general for the solvolysis of vinyl derivatives it can be suggested that the relationship between routes A, B, and C is as follows.

Route B. The rate is strongly dependent upon the H^+ concentration of the reaction media.

Route A. The rate should be almost independent of the solvent pH.

Route C should exhibit increasing rates with increasing concentration on base, but is limited to certain structural features of reactant as mentioned above.

From the available data it is difficult to predict the relative values of the corresponding *k*'s, but it can be concluded that several mechanisms may operate, and the addition–elimination route may be important for some compounds in acidic media, but the SN1 route operates under nonacidic conditions. The dependence of the solvolysis rate upon H^+ concentration may be in future work an easy way to distinguish between the possible mechanisms.

Acknowledgments. We are indebted to Drs. W. M. Schubert, University of Washington, G. Modena, University of Padova, and R. G. Bergman, California Institute of Technology, Pasadena, Calif., for communicating their unpublished results.

(7) A. G. Martinez, M. Hanack, R. H. Summerville, P. v. R. Schleyer, and P. J. Stang, *Angew. Chem.*, **82,** 323 (1970).

(8) See Table I, footnote *pp*.

(9) See Table I, footnote *bb*.

(10) A. Ghenciulescu, N. Youssif, and M. Hanack, unpublished results.

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Molecular Dynamics of π–π Complex Formation by Deuterium Quadrupolar Relaxation[1]

Sir:

π–π complexes between an electron donor molecule (D) and an acceptor molecule (A) (EDA complexes)[2] have been extensively studied in recent years.[3–6] How-

(1) Nuclear Relaxation and Molecular Properties. IV; part III: Ch. Brevard, J. P. Kintzinger, and J. M. Lehn, *Chem. Commun.*, 1193 (1969).

(2) No assumption about the electronic structure of these complexes is made here. See R. S. Mulliken and W. B. Person, *J. Amer. Chem. Soc.*, **91,** 3409 (1969); M. J. S. Dewar and C. C. Thomson, Jr., *Tetrahedron, Suppl.*, **7,** 97 (1966).

(3) G. Briegleb, "Elektronen Donator-Acceptor Komplexe," Springer-Verlag, Berlin, 1961.

(4) L. J. Andrews and R. M. Keefer, "Molecular Complexes in Organic Chemistry," Holden-Day, San Francisco, Calif., 1964.

(5) N. J. Rose, "Molecular Complexes," Pergamon Press, New York, N. Y., 1967.

(6) R. Foster, "Organic Charge Transfer Complexes," Academic Press, London, 1969.

Table I. Relaxation Times and Rate Constants for Dynamical Processes in π–π Complex Forming Systems[a]

System	Range of α	K_c, l. mol^{-1}	T_q^f,[b] msec	T_q^c,[b] msec	k_f,[c] nsec^{-1}	k_c,[c] nsec^{-1}	k_a,[c] l. M^{-1} nsec^{-1}	k_d,[c] nsec^{-1}
[TNB, F]	0–0.42	1.0	220	35	94	15	15	15
[TNB, MF]	0–0.32	0.8	140	20	60	8.5	6.1	7.6
[TNB, MPh]	0–0.22	3.5	180	20	77	8.5	17	5.3

[a] See text and ref 15 for the definitions of the symbols and experimental conditions. [b] Deuterium relaxation time in the free and complexed D molecules in milliseconds. [c] Time in nanoseconds = 10^{-9} sec.

ever, not much is known about the molecular dynamics of the EDA systems, in particular about the rates of reorientation and lifetimes of the EDA complexes.[6] These processes are expected to be very rapid and to fall into the fast range of relaxation methods.[7–12]

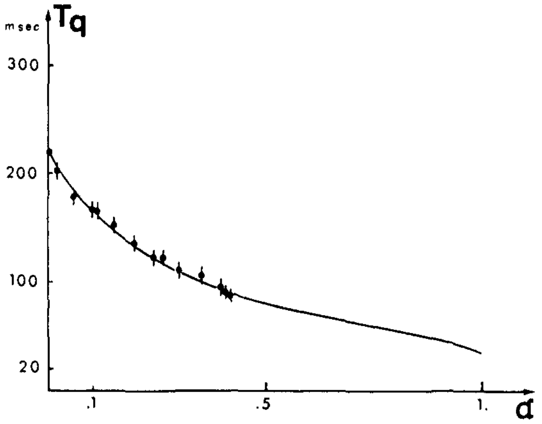
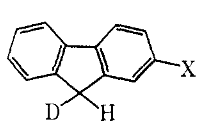
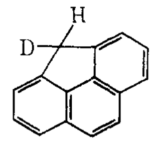


Figure 1. Experimental (points) and calculated (curve) dependence of deuteron relaxation time T_q^D on complexed fraction α in the [TNB, F] system. The calculated curve corresponds to the parameter values given in Table I.

We present here preliminary results of the first study of the molecular dynamics of EDA complex formation between 1,3,5-trinitrobenzene (TNB) and three aromatic donor molecules: fluorene-d_1 (F), methylfluorene-d_2 (MF), and methylenefluorene-d_1 (MPh), using deuterium quadrupolar labeling.[1]



F, X = H
MF, X = CH_2D



MPh

Deuteron relaxation is dominated by the efficient quadrupolar relaxation (QR) mechanism. The QR time T_q^D is given by $1/T_q^D = (3/8)(e^2qQ/\hbar)^2 f(k)$ $(e^2qQ/\hbar$ = quadrupolar coupling constant of the deuterium nucleus), where f(k) is a certain function of the rate processes in which the molecule (bearing the deuterium label) takes part.

In a system where the deuterium-labeled molecule (here the donor D) undergoes exchange between a free and a complexed state.

$$A + D \underset{k_d}{\overset{k_a}{\rightleftharpoons}} AD$$

T_q^D depends on the rate constants k_f for the reorientation[13] of free D molecules ($k_f = \tau_f^{-1}$, where τ_f is the correlation time for the free molecule), k_c for the reorientation[13] of complexed D molecules ($k_c = \tau_c^{-1}$), k_a for A + D association, and k_d for dissociation of the AD complex.

Anderson and Fryer[14] have recently given the expressions relating nuclear relaxation times to the four parameters k_f, k_c, k_a, and k_d. These equations[14] may be readily adapted for quadrupolar relaxation. It is then possible to calculate T_q^D as a function of the fraction α of complexed D molecules for a certain set of values of the four parameters. k_f and the equilibrium constant $K_c = k_a/k_d$ may be measured independently, thus leaving two unknowns, k_c and one of the rates k_a or k_d. Fitting then the theoretical curve T_q^D = f(α) to the experimental values of T_q^D, determined here by line-shape analysis of the resonance of the proton coupled to the deuteron,[1] leads to the values of the two remaining parameters.[15]

Addition of increasing amounts of TNB to a solution of F in $CDCl_3$ leads to a line-shape change of

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(7) Some recent dielectric relaxation studies[8–11] lead to values of the relaxation time of the complex and to rough estimates of its lifetime.

(8) G. W. Nederbragt and J. Pelle, *Mol. Phys.*, **1**, 97 (1958).

(9) J. E. Anderson and C. P. Smyth, *J. Amer. Chem. Soc.*, **85**, 2904 (1963).

(10) V. L. Brownsell and A. H. Price, "Molecular Relaxation Processes," Special Publication No. 20, The Chemical Society, London, 1966.

(11) R. A. Crump and A. H. Price, *Trans. Faraday Soc.*, **65**, 3195 (1969); **66**, 92 (1970).

(12) E. F. Caldin, "Fast Reactions in Solution," Blackwell, Oxford, 1964; M. Eigen and L. De Maeyer in "Technique of Organic Chemistry," Vol. VIII, Part II, 2nd ed, S. L. Friess, E. S. Lewis, and A. Weissberger, Ed., Interscience, New York, N. Y., 1963, p 895.

(13) In a first approximation the reorientations are assumed to be isotropic.

(14) J. E. Anderson and P. A. Fryer, *J. Chem. Phys.*, **50**, 3784 (1969). (In eq 5 in this reference a minus sign should replace the *plus* sign in the brackets of the Q_- and Q_+ expressions.) The influence of exchange rates on relaxation times has also been considered by H. G. Hertz, *Ber. Bunsenges. Phys. Chem.*, **71**, 979 (1967); D. Beckert and H. Pfeifer, *Ann. Phys.* (*Leipzig*), [7] **16**, 262 (1965).

(15) The present preliminary results have been obtained on an A-60 spectrometer on *ca.* 1 *M* solutions of D in $CDCl_3$ (at 33°) containing increasing amounts of TNB. The accuracy of the numerical values obtained depends on the width of the range of α values for which T_q^D could be determined experimentally. More accurate results will be obtained on a more sensitive spectrometer.[16] A comparative study of a 1 *M* and a 0.5 *M* solution of F showed that the concentration of the solution does not affect the results in the range studied here.

Line-shape analysis of the –C*H*D– resonances has been performed by the method used in earlier work.[1,17] k_f has been obtained on a 1 *M* solution of pure F, MF, and MPh.

A 1:1 stoichiometry has been obtained for the [TNB, F] complex by the method of Job[18] using chemical shift data.[16] The same stoichiometry has been assumed for MF and MPh. The equilibrium constants K_c (Table I) have been obtained from the chemical shift changes due to complex formation[6] using a least-squares method.[16] The theoretical curves T_q^D = f(α) have been fitted to the experimental results using the program QUADEX[16] and an IBM 360/44 computer.

(16) To be described in the final account of this work.

(17) J. P. Kintzinger, J. M. Lehn, and R. L. Williams, *Mol. Phys.*, **17**, 135 (1969).

(18) P. Job, *C. R. Acad. Sci.*, **180**, 928 (1925).

the –C*HD*– resonance, whose triplet fine structure due to H,D coupling dissappears progressively. Line-shape analysis[1,17] gives T_q^D for various values of α.[15] Similar results are obtained for the [TNB, MF] and the [TNB, MPh] systems. Treatment of the data as described above leads to the values listed in Table I. The figure shows the experimental $T_q^D = f(\alpha)$ points and the corresponding best fitted theoretical curve for the [TNB, F] system.

Several conclusions may be drawn from these results (see Table I). (1) The rate of reorientation of the complexed D molecules, k_c, is much slower than that of the free molecules, k_f. Thus the complex behaves as a specific AD entity which undergoes reorientation as a single, discrete unit.[19] Using the Debye relation $\tau = 4\pi\eta a^3/3kT$ (with τ = rotational correlation time, a = radius of the rotating unit, and η = viscosity of the solution),[20] one finds that the "radius" of the [TNB, F] complex is *ca.* 1.8 times larger than that of the free F molecule. This result agrees with the fact that the TNB and F molecules are of comparable average "size" and that the distance between the TNB and F components in the complex should be of the order of 3.5 Å as in the [TNB, naphthalene] complex for instance.[21]

(2) The rate processes occurring in the present EDA systems are very fast (*ca.* 10/nanosecond (nsec) = 10^{10} sec^{-1}). The analysis of nuclear relaxation data (in particular of the quadrupolar type) may thus be a powerful method for studying extremely fast reactions (see also ref 14 and 19).

(3) The rate of dissociation, k_d, of the AD complex is comparable to its rate of reorientation, k_c, and is much slower than the rate of reorientation of free D molecules (k_f). In other words, the lifetime of the complex (k_d^{-1}) is longer than the correlation time for rotational motion of the free D molecules (k_f^{-1}) but is comparable to the correlation time of the complex (k_c^{-1}). The complex may be considered as being of the "collision complex" type ("contact charge-transfer" complexes of Mulliken and Orgel[22]).

(4) The correlation time of the –CH_2D group in MF is not affected by complex formation as may be expected from the rapid rate of internal rotation about the C–CH_2D bond which effectively decouples the motion of the –CH_2D group from the overall molecular reorientation.[1]

The present studies are being extended to other systems, especially to some more stable complexes, in order to arrive at a precise description of the molecular dynamics of complex formation. The application to ion-pair formation and to biological systems[23] (molecular dynamics of enzyme-substrate, drug-receptor model interactions) is also in progress.

(19) J. E. Anderson, *J. Chem. Phys.*, **51**, 3578 (1969).

(20) The Debye relation applies for spherical units undergoing isotropic reorientation. This is a gross approximation in the present case but allows, nevertheless, qualitative comparisons to be made.

(21) S. C. Wallwork, *J. Chem. Soc.*, 494 (1961).

(22) R. S. Mulliken and L. W. Orgel, *J. Amer. Chem. Soc.*, **79**, 4839 (1957).

(23) J. P. Behr, H. Goldwhite, and J. M. Lehn, unpublished results.

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Solvation Studies of Sodium and Lithium Ions by Sodium-23 and Lithium-7 Nuclear Magnetic Resonance

Sir:

In connection with a detailed study of ionic solvation carried out in this laboratory, it was decided to investigate the nuclear magnetic resonances of alkali metal ions in various solvents. This communication reports the results obtained with ^{23}Na nmr as well as some preliminary results observed with ^{7}Li nmr. Literature search indicated that such studies have been rather sparse, especially in nonaqueous solvents. The most detailed study found was that of Bloor and Kidd,[1] who measured the influence of solvents on the chemical shifts of ^{23}Na with respect to aqueous solutions. However, only sodium iodide was used as solute, and it was of interest to us to extend the studies to other sodium salts in order to observe possible influence of the anion on solvation.

A Varian DA-60 in wide-line configuration was modified to allow the recorder sweep potentiometer to sweep the magnet power supply for the ^{23}Na investigations at 15.9 MHz. Natural line widths for the ^{23}Na resonances are such that the use of 15-mm nonspinning samples did not significantly degrade our results. Shifts were calibrated using the side-band technique with a saturated solution of sodium chloride in water as the standard.

For the ^{7}Li investigations, the DA-60 was run in its normal locked configuration at 24.29 MHz. A saturated aqueous solution of lithium chloride was used as a standard.

Four sodium salts were thus far investigated, tetraphenylborate, perchlorate, iodide, and thiocyanate. It was immediately obvious that the nature of the anion plays a very important role in the resulting chemical shift. Confirming the results of Bloor and Kidd, the chemical shifts for sodium iodide solutions were concentration dependent. Likewise, the magnitudes of the chemical shifts and their solvent dependence were, in general, in good agreement with the previous results.[1] Chemical shifts for sodium thiocyanate were also concentration dependent, although to a lesser extent than those for the iodide.

A very different behavior, however, was found for the tetraphenylborate and the perchlorate. For example, the ^{23}Na resonance of the tetraphenylborate solutions in tetrahydrofuran, ethyl acetate, acetone, acetonitrile, and methanol did not show any concentration dependence in the 0.5–0.1 M concentration range. Only in nitromethane solutions was there a slight ($\sim$10 Hz) shift downfield with dilution. Corresponding solutions of sodium iodide were much more concentration dependent, with downfield shifts of $\geq$30 Hz for the same dilution. Likewise, the solvent dependence of the chemical shift (with reference to aqueous solutions) is quite different for the two salts, as seen from the data in Table I.

It seems reasonable to ascribe this difference in behavior of the four salts to the formation of ion pairs in the case of the iodide and, to some extent, of the thiocyanate. Thus, for the tetraphenylborate and the perchlorate the changes in the chemical shift of the cation are due only to changes in the shielding brought

(1) E. G. Bloor and R. G. Kidd, *Can. J. Chem.*, **46**, 3425 (1968).