precursor compounds, as well as the corresponding ring protons in mesitylene. The same protons in the monomesitylcarbonium ion **6** are somewhat more deshielded by its cationic charge but to a significantly lesser extent than those in the unmethylated diarylcarbonium ions **4** and **5**. (f) Finally, the methinyl proton at the carbonium ion center in **1** may be regarded as significantly deshielded in comparison to its chemical shift (value) in the tetracovalent precursor **1a** (τ 2.37 *vs.* 3.80); however, it is markedly less deshielded than in **6** and in the less stable[4] diphenylcarbonium ion (τ 0.19),[5] suggesting a much higher level of positive charge localized at this methinyl carbon in **4** and **6**.

Several novel conclusions may be drawn from these observations. For one, the magnetic equivalence of the *o*-methyl protons in all the dimesityl compounds examined, as well as their higher field positions relative to the *para* protons, suggests that the *o*-methyl groups are capable of ready exchange of their environments even at temperatures as low as $-60°$. At this temperature hindered rotation about the bond linking the carbonium ion center to the mesityl ring in **6** has been observed.[1] Nonetheless, relatively unrestricted internal rotations (about the same bond) in the dimesityl ions **1** and **2** and their precursors, which permit each of the *o*-methyl groups unhindered movement in and out of the shielding cone of the other ring, must be recognized in describing the motions of the two rings. Such rotational modes correlate both with the greater shielding of the two *o*- (*vs.* the *p*-) methyl groups as well as their magnetic equivalence.

An attractive possibility, on the basis of which we have undertaken feasibility computations, corresponds to intramolecular rotation involving the coordinated motion of the two mesityl rings. Herein it is assumed they both rotate with the same angular velocity about the bonds connecting them to the central carbon, and they are so arranged that, when one group lies in the plane formed by the central carbon and its bonds, the other is in a plane perpendicular to it. Internuclear distances between nonbonded atoms were calculated for a variety of conformations. Two types of hybridization (sp^3 and sp^2) of the central carbon atom and only normal values of the C–C and C–H bond lengths were considered. A single pair of methyls, one from each ring, was chosen, since the relative conformation of a methyl pair can be obtained from that of another pair by rotation through a suitable value of θ. The results of such calculations are the following: minimum carbon–carbon distances 3.39 Å at $\theta = 9°$ (sp^3) and 3.59 Å at $\theta = 0°$ (sp^2); minimum hydrogen–hydrogen distances 2.14 Å at $\theta = 18°$ (sp^3) and 2.37 Å at $\theta = 12°$ (sp^2).

Recalling the value of the van der Waals radius of hydrogen (1.2 Å) an overlap (encounter) during rotation (at 2.4 Å or less) could not be excluded for either the sp^3 or sp^2 case, though it would never be really severe for the latter. However, if further coordination in the rotation is assumed, the overlap clearly could disappear. Calculations were then performed in which both methyls were rotated 60° about the symmetry axis corresponding to the hydrogens' *getting out of each other's way without disturbing the carbon frame.* The results here show that when only one methyl is rotated, the hydrogen–hydrogen distances are more than adequate to allow full rotational clearance (2.64 and 2.83 Å at $\theta = 18°$ (sp^3) and 2.87 and 3.03 Å at $\theta = 12°$ (sp^2) depending on which methyl is rotated). If both are rotated, the departure from overlap is very much increased; consequently, the coordinated rotation of the mesityl rings is quite feasible and is assured, if some concomitant coordination in the internal rotation of a methyl group is permitted. For obvious reasons, we refer to these conditions which appear to satisfy the observed properties of the highly hindered system considered above as the "cogwheel effect." Further discussion of the other observations noted here for the dimesitylcarbinyl system is reserved for the occasion of a more definitive article in the near future.

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(5) See footnote *e*, Table I.

Identification of Collision-Induced Fragmentation Pathways by Ion Cyclotron Double Resonance

Sir:

The utilization of mass spectrometry for the solution of several research problems has been based on the ability to predict, identify, and measure the degree of fragmentation of specific ions.[1,2] Detailed information regarding fragmentation processes at low pressure (10^{-8} torr) has come mainly from the study of series of compounds, including specifically labeled species, and by examination of metastable peaks. Intramolecular decompositions, induced by the collision of an ion with a neutral molecule, have not been extensively exploited for studying the nature of complex ions.[3,4] We now wish to describe a convenient technique, ion cyclotron double resonance,[5–7] for identifying collision-induced fragmentation pathways. This technique provides a useful method for exploring the character of specific ions.

At high pressures (10^{-5} torr) it becomes highly probable that ions collide with neutral molecules and that the equations of motion of related ions, such as parent and daughter ions (eq 1), are coupled.[8] Since ion–

$$M\cdot^{+} + \text{neutral} \xrightarrow{k} [M - A]^{+} + A\cdot + \text{neutral} \qquad (1)$$

molecule reaction rate constants are dependent on relative ion–molecule velocities, heating an ion with a radiofrequency electric field of the order of 0.05 V/cm will result in measurable changes in the concentrations

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(1) H. Budzikiewicz, C. Djerassi, and D. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, Inc., San Francisco, Calif., 1967.

(2) W. Pike and F. McLafferty, *J. Am. Chem. Soc.*, **89**, 5953 (1967).

(3) C. Melton in "Mass Spectrometry of Organic Ions," F. McLafferty, Ed., Academic Press Inc., New York, N. Y., Chapter 2, reviews high-energy (>2 keV) collision-induced dissociations.

(4) F. Field, *Accounts Chem. Res.*, **1**, 42 (1968), discusses chemical ionization mass spectrometry where the ionization and fragmentation of a neutral substance are effected by reaction with an ionized reagent.

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

(6) J. Beauchamp, L. Anders, and J. Baldeschwieler, *J. Am. Chem. Soc.*, **89**, 4569 (1967).

(7) J. Baldeschwieler, *Science*, **159**, 263 (1968).

(8) J. Beauchamp, *J. Chem. Phys.*, **46**, 1231 (1967); J. Beauchamp, Ph.D. Thesis, Harvard University, 1968.

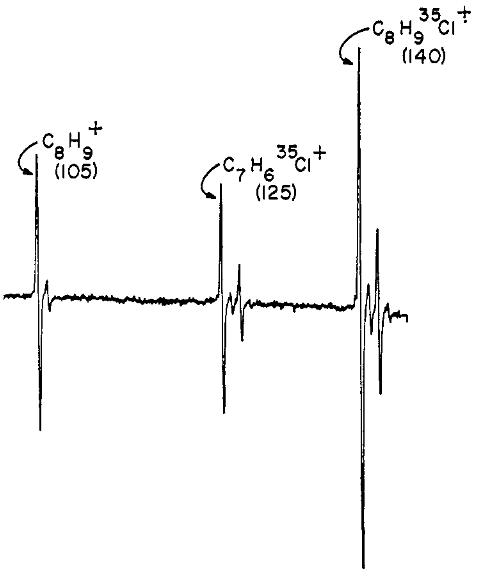


Figure 1. Single-resonance spectrum of a 10:1 mixture of nitrogen to *p*-chloroethylbenzene obtained at 1×10^{-5} torr with an ionizing energy of 15 eV. The derivative mode line shape is the result of magnetic-field modulation with phase-sensitive detection.

of other ions in equilibrium with the irradiated ion.[9] It is possible to observe this coupling by ion cyclotron double-resonance techniques. Pulsed double-resonance spectra[6] directly show the change in the intensity (increase or decrease) of an observed ion as different *m/e*'s are irradiated. The sign and magnitude of the observed double-resonance signal provide information concerning the variation of the reaction rate constant with ion energy, dk/dE_{ion}.[10]

An unimpeachable example will be used to illustrate the technique for identifying collision-induced fragmentation pathways. The ion cyclotron single-resonance spectrum of *p*-chloroethylbenzene[11] at 1×10^{-7} or 1×10^{-5} torr obtained at an ionizing energy of 70 eV is similar to the mass spectrum obtained at 10^{-8} torr with a conventional sector spectrometer.[12] Introduction of a low-mass, relatively unreactive neutral species such as nitrogen as a dilutant and collision partner does not appreciably alter the spectrum and serves to prevent the occurrence of additional peaks when reactive neutrals are present. The single-resonance spectrum of a 10:1 mixture of nitrogen to *p*-chloroethylbenzene obtained at 1×10^{-5} torr with an ionizing energy of 15 eV is shown in Figure 1.[13] Figure 2a shows the pulsed double-resonance spectrum (changes in intensity) of *m/e* 105, while a pulsed irradiating field is swept through *m/e* 125, 127, 140, and 142. An increase in the intensity (usually associated with an endothermic reaction)[10] occurs as *m/e* 140 and 142 are heated; however, no change occurs as *m/e* 125 and 127 are heated. Therefore only

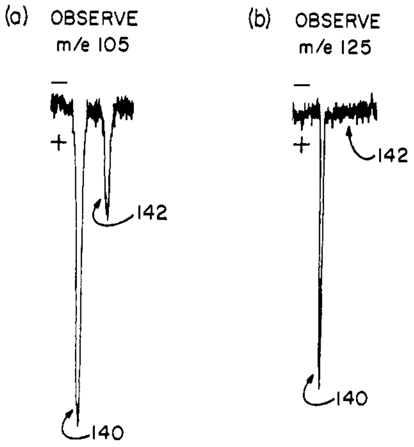
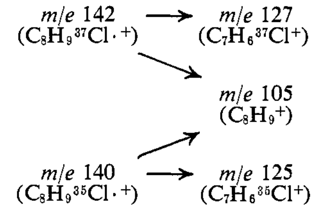


Figure 2. Pulsed double-resonance spectra of (a) *m/e* 105 where *m/e* 125, 127, 140, and 142 are irradiated and (b) *m/e* 125 where *m/e* 105, 140, and 142 are irradiated. A + contribution represents an increase in the intensity of the observed ion.

m/e 140 and 142 are coupled to 105. The relative contributions to *m/e* 105 from *m/e* 140 and 142 in the double-resonance spectrum (3:1) are the same as the ratio of the intensities of these peaks in the single-resonance spectrum. A difference in dk/dE_{ion} would not be expected for isotopic species which undergo similar fragmentation.

Figure 2b proves that *m/e* 125 is being generated only from *m/e* 140 and that there is no contribution from *m/e* 142. It is important to note that both the presence and absence of fragmentation pathways can be substantiated in a single experiment. The fragmentation behavior of *p*-chloroethylbenzene elucidated by ion cyclotron double-resonance techniques is summarized in Scheme I.

Scheme I



The experimental results are in complete accord with anticipated results and clearly demonstrate that it is possible by ion cyclotron double-resonance techniques to detect changes in fragment ion concentrations by inducing ion–molecule collisions. If intramolecular decompositions induced by collision with a neutral molecule parallel those induced by electron impact, it thus may become possible in a complex spectrum to determine all sources of a given ion and to determine completely all subsequent decomposition pathways leading to peaks of finite intensity. On the other hand, metastable peaks, which are dependent on decompositions in the field-free region of a sector mass spectrometer, can arise only for ions with a half-life of the order of 10^{-6} sec. These peaks are rarely available for the identification of all fragmentation pathways. Further studies in this area are now in progress.

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[9] The determination of the absolute ion energy distribution is difficult and depends on several factors; however, it may be readily varied from above thermal energies to approximately 15 eV.[8,10]

[10] J. Beauchamp and S. Buttrill, *J. Chem. Phys.*, 48, 1783 (1968).

[11] We wish to thank Dr. R. Hettler of Dow Chemical Co. for the sample of *p*-chloroethylbenzene.

[12] F. McLafferty, *Anal. Chem.*, 34, 16 (1962).

[13] Experiments identifying collision-induced fragmentation pathways in *p*-chloroethylbenzene could be carried out equally well at 70 or 15 eV in the presence or absence of nitrogen. At an ionizing energy of 70 eV, major peaks at *m/e* 28 ($N_2{}^{\cdot +}$) and 29 (N_2H^+) appeared in the spectrum.

gratefully acknowledged. The author wishes to thank Dr. J. D. Baldeschwieler and Messrs. S. Buttrill, R. Dunbar, and J. Garcia for many helpful discussions.

[14] Public Health Service Special Fellow on sabbatical leave from the University of Cincinnati, 1967–1968.

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On the Mechanism of Complex Formation and Solvent-Exchange Reactions of Iron(3+) in Dimethyl Sulfoxide[1]

Sir:

Complex formation reactions of 3+ aquo metal ions such as Fe^{3+} and Al^{3+} have presented special problems to chemical dynamicists. Apparent rate sensitivity to entering ligands (basicity dependence) suggests an *associative* mode of activation[2] in an octahedral substitution, but there is a "proton ambiguity." No kinetic test distinguishes paths 1 and 2. Seewald and Sutin[3]

$$\mathrm{Fe(OH_2)_6^{3+} + X^- \longrightarrow Fe(OH_2)_5X^{2+} + H_2O} \qquad (1)$$

$$\mathrm{Fe(OH_2)_5OH^{2+} + HX \longrightarrow Fe(OH_2)_5X + H_2O} \qquad (2)$$

and Carlyle and Espenson[4] have produced ingenious indirect arguments supporting path 2 in some cases. If they are right, Fe^{3+} falls within the common *dissociative* pattern of octahedral substitution.

For the light they may shed on the "proton ambiguity," reactions of Fe^{3+} in dimethyl sulfoxide (DMSO) should be interesting. DMSO is an *aprotic* solvent in which metal ions have been shown to display kinetic behavior similar to their behavior in water.[5,6]

We have prepared $Fe(DMSO)_6(NO_3)_3$ by heating $Fe(NO_3)_3 \cdot 6H_2O$ in DMSO. Lemon yellow crystals form on cooling which may be recrystallized from DMSO. *Anal.* Calcd for $FeC_{12}H_{36}O_9S_6N_3$: C, 20.30; H, 5.11; N, 5.91. Found: C, 19.89; H, 5.09; N, 5.99. Reactions of $Fe(DMSO)_6^{3+}$ with SCN^- (ionic strength 0.024 maintained with $NaNO_3$) and sulfosalicylic acid (SSA) were examined at 25° in a Durrum stopped-flow spectrophotometer using wavelengths of 446 and 536 mμ, respectively. Since rates of approach to equilibrium were observed, the equilibrium constants for complex formation were estimated *via* the Newton and Arcand procedure[7] from more accurate spectrophotometric data obtained using a Gilford 240 manual spectrophotometer. All experiments were carried out using excess $Fe(DMSO)_6^{3+}$ to ensure pseudo-first-order kinetics and/or only monocomplex formation. Experimental concentration ranges were: Fe^{3+}, $1\text{-}4 \times 10^{-3}\ M$; ligand, $1\text{-}6 \times 10^{-4}\ M$.

We report over-all equilibrium constants for complex formation (precise to ∼5%) and second-order rate constants for complex formation as follows: SCN^-, 1180 M^{-1} and 670 ± 10 M^{-1} sec^{-1}; SSA, 420 M^{-1} and 23 ± 4 M^{-1} sec^{-1}.

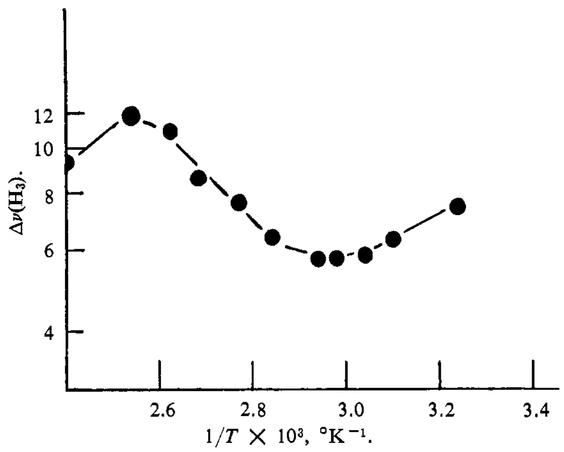

Figure 1. Paramagnetic broadening of DMSO proton resonance by Fe^{3+} as a function of temperature. Data are reported for 0.01 and 0.02 M solutions and presented normalized to 0.02 M.

Proton magnetic resonance spectra of DMSO and DMSO containing 0.01 and (at higher temperature) 0.02 M $Fe(DMSO)_6^{3+}(NO_3)_3$ were recorded as a function of temperature. Paramagnetic line broadening (line width corrected for ∼1.5 Hz pure solvent line width) as a function of $1/T$ is presented in Figure 1 normalized to 0.02 M Fe^{3+}. The observed broadenings are small for precise analysis since they are precise to ±0.2 Hz (solubility limitations prevent study of higher concentrations). An "Arrhenius region" is seen between about 80 and 100°. Following established procedures,[8] including correction for the low-temperature outer-sphere broadening, a solvent-exchange rate constant of 1400 ± 200 sec^{-1} is estimated for 100°. The activation energy, E_a, is 10 ± 2 kcal/mole; thus the solvent-exchange rate at 25° is estimated to be approximately 50 sec^{-1}. These values relate to the corresponding ones for H_2O exchange as might have been expected.[5,6]

According to Eigen's[9] mechanism, a complex formation reaction is written as

$$\mathrm{Fe(DMSO)_6^{3+} + L^{n-}} \overset{K}{\rightleftharpoons} \mathrm{Fe(DMSO)_6^{3+},L^{n-}} \xrightarrow{k_1} \mathrm{Fe(DMSO)_5L^{(3-n)+} + DMSO} \qquad (3)$$

Observed second-order rate constants, k_2, are interpreted as $k_2 = Kk_1$, where K is the equilibrium constant for outer-sphere association, and k_1 is the first-order rate constant for outer-sphere to inner-sphere conversion. For neutral ligands, K is expected to be of the order of unity. Using Fuoss' theory[10] and an ion size parameter of 5 Å, K for SCN^- is estimated to be 106 (at ionic strength 0.024). The k_1 values may then be *approximated* for the various ligands as: DMSO, 50 sec^{-1}; SCN^-, 6.3 sec^{-1}; SSA, 23 sec^{-1}. The clustering of these values suggests substitution insensitive to entering ligand and a normal *dissociative* mode of activation.

We are examining other ions. Negative $\Delta S^{\neq}$ values have recently been cited as evidence of the *associative*

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[1] We acknowledge with thanks the support of the National Research Council of Canada.

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[10] R. M. Fuoss, *J. Am. Chem. Soc.*, 80, 5059 (1958).