2.7, in good agreement with the accepted value of 2.83.[5] Moreover the ORD and CD curves we obtain from this partially photoresolved complex agree with the published ones.[5,6]

Photoresolution rate curves for *cis*-dioxalatodiaquochromate and the dimer form, di-μ-hydroxy-tetraoxalatodichromate, are shown in Figures 2 and 3. These curves are quite similar to those of Figure 1, for similar reasons. However, in both cases an additional photoreaction must be included: *cis–trans* isomerization in the first case and isomerization between *meso* and enantiomeric forms in the second. ORD–CD curves very similar to that for the tris complex were obtained for these compounds. Because of the additional complexity of the kinetics, rate constants and the value of the dissymmetry factor have not been determined yet. We report also the interesting case of photolytically induced optical activity in the *trans*-dioxalatodiaquochromate isomer, also in Figure 3. Presumably this occurs through photoconversion to the *cis* isomer which then photoresolves, but our data indicate that this does not proceed to the same equilibrium as that obtained when starting with the same concentration of pure *cis* complex.

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[5] A. J. McCaffery, S. F. Mason, and R. E. Ballard, *J. Chem. Soc.*, 2883 (1965).

[6] J. P. Mathieu, *J. Chim. Phys.*, 33, 87 (1936).

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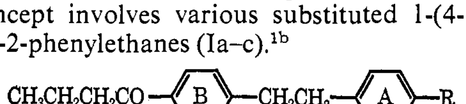
Charge Migration in Molecular and Fragment Ions

Sir:

Recent investigations[1,2] have produced considerable evidence for the notion[3] that the unimolecular decomposition of ions in a mass spectrometer requires the presence of a positive charge at the site of fragmentation. This has led to the concept of "charge localization" at the point of lowest ionization potential in the molecular ion where it then triggers fragmentation.

One of the most recent examples designed to prove this concept involves various substituted 1-(4-butyrophenyl)-2-phenylethanes (Ia–c).[1b]



Ia, R = NO_2
b, R = NH_2
c, R = $CH_3CH_2CH_2CO$

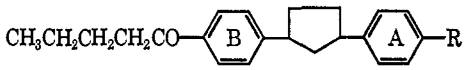
Indeed Ia exhibits intense peaks due to loss of ethylene ("McLafferty rearrangement") or propyl (acyl cleavage) from the substituent on ring B while these are almost completely absent in the spectrum of Ib because the positive charge is thought to reside in ring B of the molecular ion of Ia, but in ring A of that of Ib. The diketone Ic does undergo both reactions, but only once, either at ring A or at ring B.

These authors[1b] consider the possibility that ionization occurs initially at any point of the molecule and it is assumed that the charge migrates rapidly to the site of lowest ionization potential where it then causes fragmentation.

The failure of Ic to undergo fragmentation at the second ketone moiety after initial decomposition of the first is cited[4,5] as evidence for charge localization in the resulting fragment ion.

We felt that this assumption of such a fixation of charge in fragment ions may be unwarranted and the situation may more closely resemble a dynamic distribution of charge which, over a period required for electron impact induced fragmentation ($<10^{-5}$ sec), is statistically maximized at the site of lowest ionization potential (*i.e.*, that the average relative charge density decreases with increasing relative ionization potential of the site).

To test this concept, the mass spectra of a series of compounds (IIa–e),[6] which eliminate the following shortcomings of the diphenylethanes (Ia–c) in this respect, were taken: (1) the absence of the C_2 bridge eliminates the undesirable competing benzyl bond cleavage (which consumes most of the molecular ions of Ib); (2) the McLafferty rearrangement of the valeryl group involves the elimination of propylene rather than ethylene, the loss of which is well known[8] to be much less favorable; and (3) the use of an N-acyl group (which by elimination of ketene results in the equivalent of the molecular ion of the corresponding amine) provides positive proof[9] that the charge is at least at one time concentrated on ring A.



IIa, R = NO_2
b, R = NH_2
c, R = $CH_3(CH_2)_3CO$
d, R = $NHCOC_2H_5$
e, R = $N(COC_2H_5)_2$

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[1] (a) F. W. McLafferty and T. Wachs, *J. Am. Chem. Soc.*, **89**, 5043 (1967); (b) T. Wachs and F. W. McLafferty, *ibid.*, **89**, 5044 (1967).

[2] H. Bruderer, W. Richter, and W. Vetter, *Helv. Chim. Acta*, **50**, 1917 (1967).

[3] F. W. McLafferty in "Determination of Organic Structures by Physical Methods," F. C. Nachod and W. D. Phillips, Ed., Academic Press Inc., New York, N. Y., 1962, p 93; J. S. Shannon, *Tetrahedron Letters*, 801 (1963); H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, Inc., San Francisco, Calif., 1967, p 9.

[4] Reference 1b, footnote 12.

[5] Formation of secondary ions which involves reaction at the second ketone moiety of Ic after initial decomposition of the first was thought to be so impossible that the low-intensity ions due to $M - C_2H_4 - C_2H_4$, $M - C_2H_4 - C_3H_7$, and $M - C_2H_4 - C_4H_9O$ in the spectrum of Ic were suggested to involve at least in part loss of C_2H_4 from the center of the molecule.[4]

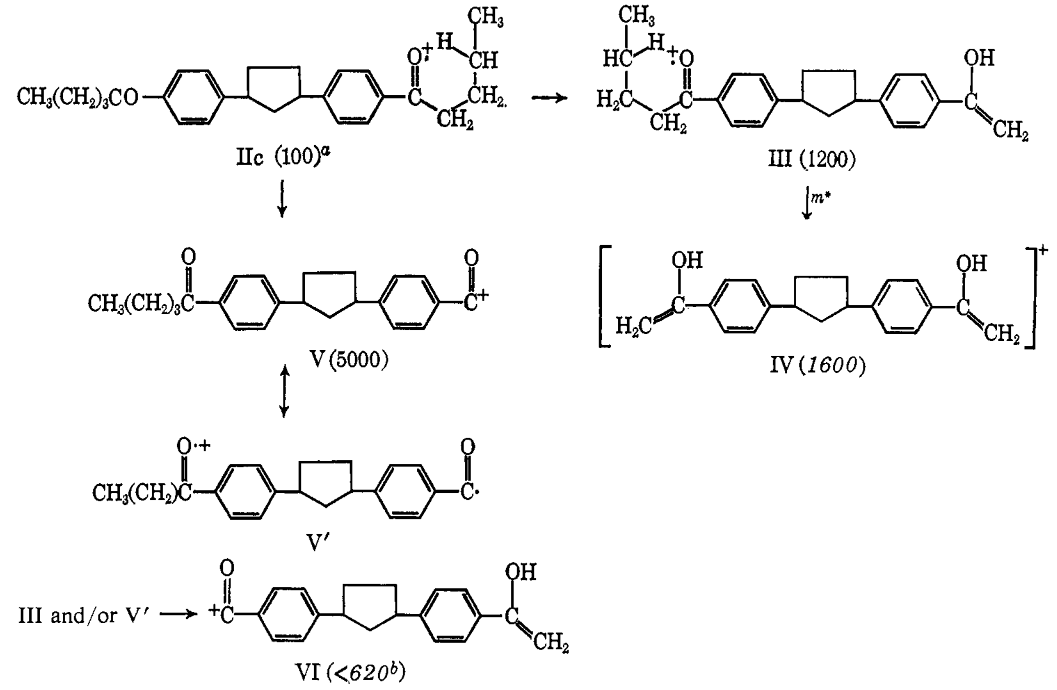
[6] Prepared from 1,3-diphenylcyclopentane:[7] IIc by acylation and IIa by partial nitration followed by acylation; IIb by reduction of IIc. Acylation of IIb with boiling propionic anhydride gave IIe, while cold anhydride in pyridine yielded IId. The spectral properties (uv, ir, nmr, and mass spectra) confirm the structures shown. The stereochemistry is not yet established and will be discussed in the full paper.

[7] S. Eskola, *Ann. Acad. Sci. Fennicae, Ser. A, II, Chem.*, No. 18 (1946). (The crude product was hydrogenated to remove unsaturated by-products).

[8] H. Budzikiewicz, C. Fenselau, and C. Djerassi, *Tetrahedron*, **22**, 1391 (1966).

[9] Assuming that charge localization is indeed a requirement for fragmentation and that it holds for the elimination of ketene just as well as for the McLafferty rearrangement,[1] acyl cleavage,[1b] and the elimination of water and acids.[2]

Scheme I



^{a} Values in parentheses refer to relative intensities ($M^+ = 100$). Values in italic type refer to ions formed by secondary fragmentation involving the other ring. ^{b} Upper limit, because VI is indistinguishable from IV − CH_3, for which a metastable peak is found.

Fragmentation of the side chain shows the same trend in IIa and IIb as was reported for Ia and Ib, and the data are in agreement with the conclusions drawn previously.[1b] A more detailed discussion of this aspect will be presented in the full paper. The mass spectrum of IIc, however, indicates, in contrast to previous finding on Ic,[4] that the elimination of propylene from ring A is followed by the same reaction of ring B (Scheme I).

Table I.^{a} Relative Abundances of Selected Ions in the Mass Spectra of IIb,d,e

	m/e								
	433	391	376	377	335	320	321	279	264
IIe	M	M − a	M − c	M − b	M − a − b	M − b − c	M − 2b	M − 2b − a	M − 2b − c
Intensity, %	100	9	45	630^b	*100*^{a}	*320*^{c}	300^b	*100*^{a,b}	*70*
IId				M	M − a	M − c	M − b	M − a − b	M − b − c
Intensity, %				100	32	85^c	75^b	*25*^{a,b}	*20*^{c}
IIb							M	M − a	M − c
Intensity, %							100	10^a	30^c

^{a} The letters a, b, and c, refer to C_3H_6, C_3H_4O, and C_4H_9 (McLafferty rearrangement, ketene elimination, and acyl cleavage, respectively); superscripts indicate a metastable peak due to the loss of the corresponding group. Italic type figures represent the relative abundance of ions formed by secondary fragmentation involving the other ring.

In the light of the concept that charge localization is the driving force for fragmentation, the above data and those summarized in Table I indicate the following: (a) the positive charge can migrate from one phenyl ring at which it has induced fragmentation to the other one to cause further fragmentation (intensities in italic type); (b) migration is the less favored the greater the difference in ionization potential[10] (McLafferty rearrangement of the valeryl group is more dominant from the M − C_3H_6 ion III of IIc than from the M − C_2H_4CO ion of IId); and (c) fragmentation requiring charge migration is more favored in odd-electron fragment ions (where it results only in transfer of one electron) than in even-electron ions (where it requires, in addition, uncoupling of an electron pair to form a diradical ion; see the lower abundance of fragments such as VI derived from the M − C_4H_9 ion V in IIc).[11] Since an even-electron fragment ion can be viewed as a radical which has lost one electron, this statement represents a special case of (b), because free radicals have relatively low ionization potentials.[12]

From the data presented in this communication, it can be concluded that the charge should not be considered as completely localized even if it has been shown to be formally present in a specific area of the fragment ion at the time of its formation. It will be free to migrate to other areas in the ion, even if they are separated by several σ bonds, as in system II, and this migration is governed by the ionization potentials of

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(10) Compare the differences in the ionization potentials of acetophenone *vs.* aniline ($\Delta IP = 1.06$ eV), acetanilide ($\Delta IP = 0.5$ eV), nitrobenzene ($\Delta IP = -0.80$ eV).

(11) The immonium ion produced from the 3β-aminoandrostane derivatives discussed in ref 3 are excellent examples for (c), and these compounds were chosen, at least intuitively, by these authors for that reason.

(12) M. Krauss and V. H. Dibeler in "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press Inc., New York, N. Y., 1963, p 118.

the various sites. The new distribution of charge will lead to secondary fragmentations at sites other than those where the primary fragmentation took place.

This concept is important not only for a better understanding of the fragmentation of ions in the gas phase but also in the interpretation of mass spectra in terms of structural information.

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Extrinsic Field Acceleration of the Magnetic Parahydrogen Conversion

Sir:

This letter is to report an example of increased reaction velocity observed on application of an extrinsic magnetic field. The reaction was the heterogeneous catalytic parahydrogen conversion which, under the conditions and as shown by the absence of measurable hydrogen–deuterium equilibration, was entirely magnetic in mechanism. The intrinsic field was supplied by chromium ions.

Three catalyst samples were investigated. These were (1) synthetic ruby (a dilute solid solution of Cr_2O_3 in α-Al_2O_3) containing 1 atom % Cr and powdered to a specific surface of 2.0 m^2 as previously described,[1] (2) a supported chromia/alumina prepared by impregnating powdered synthetic sapphire (α-Al_2O_3) of specific surface 2.0 m^2 with the appropriate volume of dilute chromic nitrate solution, followed by drying and ignition in air at 500° for 2 hr, giving a sample containing 0.0028 wt % Cr_2O_3; and (3) a similar supported sample containing 0.045% Cr_2O_3.

The samples were placed in turn in a quartz reactor between the poles of an electromagnet and arranged for measurement of the orthohydrogen:parahydrogen concentration ratio, as described.[1] About 0.20 g of sample was used, and each sample was heated *in situ* in flowing hydrogen for 2 hr at 500° and then quenched to room temperature so as to prevent poisoning of the paramagnetic sites by chemisorbed hydrogen. (This procedure of quenching is equivalent to, and more convenient than, evacuation and cooling from 500°.) The hydrogen used was first passed through a palladium–silver purifier, then converted to 1:1 orthohydrogen:parahydrogen over a commercial chromia catalyst at −196°, and passed over the sample at 35 ml min^{-1}.

Figure 1 shows the parahydrogen conversion rate in µmoles of orthohydrogen formed per minute over each of the three samples, at zero field and at a field of 2000 Oe. The fractional rate increase on application of the field is stated. Figure 2 shows the percentage increase of conversion rate for the 0.0028% sample as a function of field strength.

The fact that the zero-field conversion rates shown follow no particular pattern is of no consequence. The

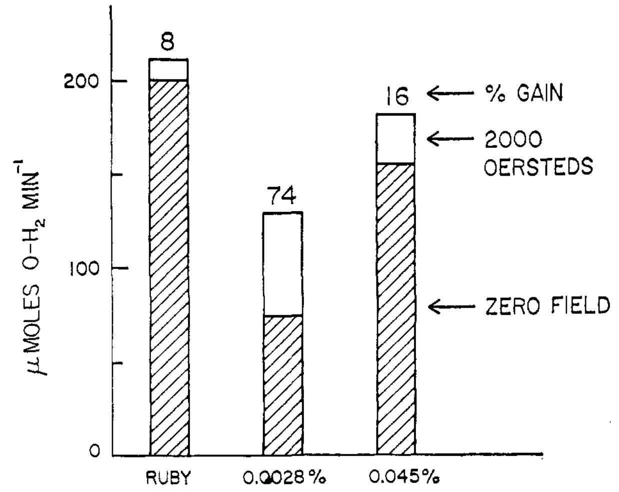

Figure 1. Increase in parahydrogen conversion rate at −100° on application of a 2000-Oe magnetic field for three chromia/alumina samples.

magnetic conversion rate is approximately proportional to $cp\mu^2/d^6$, where c is the number of paramagnetic species in the sample, p is the fraction accessible to molecular hydrogen, μ is the magnetic moment, and d the distance of nearest approach. In ruby the chromiums are isolated, but only a small and uncertain fraction is accessible. In the impregnated samples all the chromium is on the surface of the sapphire, but the fraction accessible depends on the cluster size; the effective magnetic moment of Cr^{3+} ions in antiferromagnetic clusters is considerably less than that in isolated Cr^{3+}.

Application of the field does not cause any change, temporary or permanent, of space velocity, and the reversible conversion rate change occurs abruptly when the field is applied or removed. The effect is observed as soon as the flowing hydrogen has had time (about 3 min) to reach the sensitive thermal conductivity cell used for analysis.

In view of these results it was thought that three possible explanations were worthy of consideration. The first is some field-induced relaxation of the normal exchange demagnetization in antiferromagnetics, but we have not been able to find any theoretical basis for this, except perhaps indirectly in the work of Néel on superantiferromagnetism.[2] The second is some form of dynamic polarization, or Overhauser effect,[3] but the much lower conversion acceleration over ruby argues against this explanation. The third possible explanation is related to the proposal of Nagaev[4] in which a large field-dependent increase of magnetic moment is predicted under certain conditions for two-dimensional layers of adsorbed paramagnetic atoms exhibiting exchange interaction. It is to be noted that our observation reported in Figure 2 confirms the field saturation effect predicted by Nagaev. Whether his predicted exponential decrease of moment with decrease of reciprocal temperature occurs can only be answered by more refined measurements, which are planned (the effect definitely is less at 25° than at −100°). It is also

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(1) P. W. Selwood, *J. Am. Chem. Soc.*, **88**, 2676 (1966).

(2) L. Néel, *Compt. Rend.*, **253**, 203, 1286, (1961).

(3) A. Abragam, "Principles of Nuclear Magnetism," Oxford University Press, London, 1961, p 392.

(4) E. L. Nagaev, *Kinetika i Kataliz*, **2**, 847 (1961).