flash distilled to remove the α,β-dimethylallyl alcohol present.

In the nmr spectrum of 1-methylcyclobutanol, the multiplets due to the protons at the 2 and 3 positions are clearly distinguishable. However, in the spectrum of the labeled 1-methylcyclobutanol from the deamination of the deuterated amine, no proton resonances were detected corresponding to the deuterated amine, no proton resonances were detected corresponding to the 3 position, and, therefore, no significant amount of **8** was found. This result *excludes* the intervention of cations **1–5** as intermediates in this reaction. It does not distinguish between classical ions and nonequilibrating nonclassical ion(s) as intermediates[9] but clearly shows that the ring closure proceeds directly to a 1-methylcyclobutyl-like cation and not a (1-methylcyclopropyl)-carbinyl-like cation.

That deamination of (1-methylcyclopropyl)carbinyl-^{14}C-amine gives 1-methylcyclobutanol with 3% of the activity in the 3 position[2] suggests that the 1-methylcyclobutyl cation is best represented as a relatively weakly delocalized bicyclobutonium ion which undergoes only slight equilibration. This interpretation is supported by the observation that 1-methylcyclobutyl methanesulfonate reacts with sodium borohydride to form a small but definite quantity of dimethylcyclopropane as well as methylcyclobutane.[10]

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[9] The argument presented for a nonclassical structure for the intermediates in these interconversions[2] has allegedly been refuted by the MO calculations of R. E. Davis, A. S. N. Murthy, and A. Ohno, *Tetrahedron Letters*, 1595 (1968). However, the substantial doubt cast on the validity of these calculations by J. E. Baldwin and W. D. Foglesong, *J. Am. Chem. Soc.*, **90**, 4311 (1968), would appear to leave the question still open. The delocalized structure proposed by the latter authors for bicyclobutonium cations is quite consonant with the results reported here.

[10] Z. Majerski, M. Nikoletic, S. Borcic, and D. E. Sunko, *Tetrahedron*, **23**, 661 (1967).

[11] National Science Foundation Predoctoral Fellow, 1960–1962.

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Operational Criteria for Concerted Bond Breaking in Gas-Phase Molecular Elimination Reactions

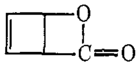
Sir:

An intriguing question often raised by mechanistically interested chemists regarding the course of molecular elimination processes concerns the details of the rate-controlling step, whether two bonds break concurrently or consecutively. A fission process is classified as stepwise or concerted depending on a postulated structure for the transition state; *i.e.*, whether at the saddle point both bonds are partially broken to a comparable degree, or whether one bond is considerably more broken than the other. Aside from the unavailability of sufficiently refined probes for exploring the structures of transition states, the relative degree of bond breaking defies quantification so that the distinction cannot be placed on an operational basis.

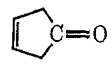
It is evident that the structure of any molecular species which has a lifetime of the order of a single vibration can be explored only indirectly, and it is equally clear that any result should be expressed in terms of rather broad distribution functions over distances, bond angles, and degrees of excitation about some average values. The magnitudes of the latter surely depend on the types of probes used. In contrast, highly sophisticated techniques are being developed for gas-phase reactions which permit the exploration of the states and structures of the *nascent products* as they emerge from the reaction complex, prior to their deactivation and relaxation to thermal equilibrium. The proposal presented here is that mechanistic questions should be formulated in terms of the geometric and energetic structures of these fragments. There is a correspondence, but not an equivalence, between this point of view and one in current use.

In the elimination of N_2 from **1**, of CO_2 from **2**, and of CO from **3**, one of the bonds in the ejected molecular fragment changes drastically during the transition from the parent to the product. When the process is a concerted one, prior to their deexcitation by collision, the distinctly separated species are comparable in energy to the transition state but they differ in their geometries (again keeping in mind that the transition state has a lifetime of the order of one molecular vibration). The excess energy is stored as geometric distortion in the products N_2, CO_2, and CO, which emerge vibrationally excited. Significantly, the vibrational coordinate for bond adjustment is essentially normal to the reaction coordinate along which bond breaking occurs, such that there is little coupling between them. Techniques are now available for detecting vibrationally excited species. In particular, $N_2^{(v)}$ and $CO^{(v)}$ readily transfer their vibrational energy to CO_2. Hence if CO_2 were added to the reaction mixture, under properly selected experimental conditions, and placed in a laser cavity, power gain should be observed as a consequence of the concerted elimination reaction. The ejection of vibrationally excited CO_2 from the bicyclic compound indicated above should be detectable directly as gain in a CO_2 laser cavity. On the other hand, if the elimination is a stepwise process (and this must be defined as a reaction in which the rate-controlling step involves the fission of one bond so that the intermediate specie has a lifetime of several molecular vibrations prior to the breaking of the second bond), the high efficiency for intramolecular energy transfer will permit the geometric relaxation of the fragment which is eventually ejected. Again, the argument hinges on the proposition that in a transition state which is chain-like, rather than ring-like, vibrations involving the bonds which require adjustment are appreciably coupled to those of the bond being broken. Since statistical energy redistribution occurs readily within highly excited molecules, when the final break occurs one may anticipate nearly equilibrated products and relatively little laser gain would be observed. Consideration of these and other examples suggests that attempts to establish for all cases sharp demarcations between concerted and stepwise processes may prove frustrating. Operationally, the anticipated difference between them for the fission say of cyclobutane into

1



2



3

two ethylenes is quantitative rather than qualitative in character.

The suggested criterion is currently pertinent relative to the dehydrohalogenation reaction. Berry and Pimentel[1] have reported their observation of $HF^{(v)}$ and consequent lasing during the elimination of the halogen acid from nascent 1,1,1-trifluoroethane.

$$CF_3 + CH_3 \longrightarrow F_3C{-}CH_3^{(v)} \longrightarrow F_2C{=}CF_2 + HF^{(v)}$$

Accordingly we point to this as an operationally demonstrated example of a concerted bond-breaking process. One may anticipate a similar mechanism for the analogous reactions.

$$NH_3 + BX_3 \longrightarrow H_3N{:}BX_3^{(v)} \longrightarrow H_2NBX_2 + HX^{(v)}$$

The rates of association of ammonia with boron trihalides are of the order 10^{-2} of collision frequencies[2,3] and are not as exothermic as those of alkyl radical recombinations. However, they do have the distinct advantage that the reagents are individually stable and available in large quantities. A suitable flow reactor with appropriate temperature control is now being constructed in our laboratory.

Direct but limited study of the states of nascent products is possible *via* molecular beam techniques. For example, in an apparatus such as was described by Wilson,[4] a beam of 1-pyrazoline could be crossed by an intense flash of photolyzing radiation. Translational velocity analyses of the rays of nitrogen and cyclopropane which are ejected at measured angles relative to the beam axis will permit deduction of the partition of energy between translation, rotation, and vibration. In turn, the angular and linear momentum conservation conditions should permit the distinction between models wherein the final fission step was stepwise or concerted. This could be more easily ascertained for a decomposition which produces three particles, as does azomethane. Kinetic processes which are thermally initiated, in contrast to photolytic reactions, could be investigated in molecular beams for which the source is shock heated. The gas dynamics of back-reflected shock-driven molecular beams is under current development.[5]

Focus on the states of excitation of nascent products will sharpen as progress is made in the calculation of the shapes of potential energy surfaces for reacting systems. In highly exothermic, three-center displacement reactions $[A + BC \rightarrow (ABC)^{\neq} \rightarrow AB + C]$, Polanyi's computations[6] support his qualitative analysis that a strongly attractive potential favors the production of vibrationally excited $AB^{(v)}$. For the more complex four-center elimination reactions symmetry correlation criteria for the lowest energy reaction path[7-9] proved to be a powerful tool for predicting stereochemical features of the decomposition process. Computational experiments with models for vibrationally distorted structures should lead to predictions of the states of excitation of the nascent species, parallel to the current development of laboratory techniques for their characterization.

Acknowledgment. I wish to acknowledge with thanks informative discussions with Professor Roald Hoffmann.

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[2] F. T. Smith and G. B. Kistiakowsky, *ibid.*, **31**, 621 (1959).

[3] S. H. Bauer, "Borax to Boranes," Advances in Chemistry Series, No. 32, The American Chemical Society, Washington, D. C., 1961, p 88.

[4] K. R. Wilson, *Discussions Faraday Soc.*, **44**, 236 (1967).

[5] G. T. Skinner and J. Moyzis, *J. Phys. Fluids*, **8**, 452 (1965).

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[7] R. F. W. Bader, *Can. J. Chem.* **40**, 1164 (1962).

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A Novel Reduction by Diiron Nonacarbonyl

Sir:

We wish to report a novel and new reaction of diiron nonacarbonyl with an unsaturated hydrocarbon in which the latter suffers reduction after initial iron carbonyl complex formation.

Treatment of 1,2,5,6-tetrabromopyracene (I)[1] with 7 mole equiv of diiron nonacarbonyl in ether (6 ml) at 25° for 1 hr produces pyracylene (II)[1] in 95% yields (Scheme I).[2] If the reaction proceeds for 15 hr, a mixture of compounds is obtained. Separation by preparative thin layer chromatography[3] reveals the presence of three components. The fastest moving component (8% yield), a reddish black crystalline solid, has a molecular weight corresponding to the formula $C_{14}H_8 \cdot Fe_2(CO)_7$ by mass spectrometry. Unfortunately, attempts thus far to obtain either an nmr or epr spectrum have been unsuccessful.[4] The mass spectrum of the second component, formed in about 40% yield, shows a molecular ion at m/e 178 (base peak), with abundant peaks at m/e 177, 176, 152, 151, and 150. The nmr spectrum[5] consists of an AB pattern for 4 H (H_A at δ 7.65, H_B at δ 7.34, with J_{AB} = 7 Hz), a singlet (2 H) at δ 7.04, and a singlet (4 H) at δ 3.49. These data identify the compound as 1,2-dihydropyracylene (III). Its ultraviolet spectrum agrees with the published data.[6] Mass spectrometry shows the final product, formed in about 50% yield, to exhibit a molecular ion at m/e 354 with a base peak at m/e 177. High-resolution data indicate its formula to be $C_{28}H_{18}$. The nmr spectrum[5] shows an AB pattern for 8 H (H_A at δ 7.70, H_B at δ 7.46, with J_{AB} = 8 Hz), two singlets of unequal intensity at δ 7.01 and 6.98 totaling 4 H, a multiplet (2 H) at δ 4.59, and a very complex multiplet (4 H) centered at δ 2.90. The ultraviolet spectrum [$\lambda_{\max}^{\text{EtOH}}$ 240 mμ (ϵ 78,270), 309 (9650), *ca.* 316 (sh; 12,060), 322 (17,790), *ca.* 328.5 (sh; 14,470), 345 (17,490), *ca.* 352 (sh; 12,970), and 360.5 (13,870)] is virtually superimposable on that of 1,2-dihydropyracyclene. This information supports the dimeric structure IV, present as a mixture of *meso* and *dl* isomers. Work-up of the reaction with D_2O leads

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[1] (a) B. M. Trost and G. M. Bright, *J. Am. Chem. Soc.*, **89**, 4244 (1967). (b) This reaction has been carried out under both nitrogen and argon. Degassing the solution by the freeze–thaw technique has no effect on the course of the reaction. If the reaction is carried out in pentane, no reduction products are obtained; only the iron carbonyl complexes are produced.

[2] *Cf.* R. Pettit, G. Emerson, and L. Watts, *ibid.*, **87**, 131 (1965); W. R. Roth and J. D. Meier, *Tetrahedron Letters*, 2053 (1967).

[3] Preparative thin layer separations were achieved using deactivated silica gel G plates with hexane elution.

[4] A structure similar to that of diiron nonacarbonyl in which two of the bridging carbons have been replaced by pyracylene can be rejected as the infrared spectrum reveals the absence of bridging carbonyls.

[5] Determined as a solution in carbon tetrachloride.

[6] A. G. Anderson and R. G. Anderson, *J. Org. Chem.*, **23**, 517 (1968).