Electron Spin Resonance Evidence for Tunneling Hydrogen Atom Transfer Reaction at 4.2 K in Organic Crystals

Sir:

We would like to report that there exists a hydrogen abstraction reaction by free radicals which proceeds even at liquid helium temperature. We believe that our results give almost conclusive evidence for the quantum mechanical tunneling process in chemical reactions. It has been pointed out by a number of workers that tunneling has to be considered in chemical reactions involving hydrogen atom transfer.[1,2] However, the concept of tunneling in chemical reactions does not seem to be widely accepted because of the following reasons.[3] It is difficult to obtain conclusive experimental evidence at ordinary temperatures since the thermally activated process greatly exceeds the contribution from tunneling. To obtain the conclusive evidence it is necessary to measure the rate constants in a wide range of temperatures, especially at low temperatures to detect the deviation from the linear Arrhenius relation. Secondly, it is necessary to show that the nonlinearity is not due to the causes other than tunneling. For example, the nonlinearity may be caused from the changes in the potential energy surface of the reaction which is due to the temperature changes in the reaction media as well as in the reactants themselves. The large mass effect is often ascribed to the tunneling effect. However, the difference in the activation energy arising from the difference in zero-point energies can give a large mass effect even on the classical rate constants in the reactions at low temperatures. The low apparent activation energy and frequency factor themselves do not give any direct evidence for the involvement of tunneling.

According to the electron spin resonance (ESR) studies reported by Kurita[4] and Lebedev et al.,[5] when single crystals of dimethylglyoxime (DMG) are irradiated by ionizing radiation at 77 K, iminoxy radical pairs J and K (see Figure 1) are formed in the specific two neighboring molecules. It is also reported that pair J converts into K at 77-100 K in the crystal of DMG-h_2 and at 190-220 K in DMG-d_2.[5a] Lebedev et al.[5a] have explained the large mass effect on the conversion rate constants by tunneling hydrogen atom transfer inside the iminoxy radical. However, the temperature ranges (20-30 K) in which the rate constants were measured are not sufficient to detect the deviation from the linear Arrhenius relation.

We have found that the radical-pair conversion proceeds even at 4.2 K in the dark. At such low temperature the thermally activated process is almost completely suppressed and the reaction can only proceed by the tunneling process. Therefore, we have measured the conversion rate constants in the temperature range from 4.2 to 140 K using the crystals of DMG-h_2 x irradiated at 77 K (see Figure 2).[6] During the course of our studies, it has been also found that the signal of the unstable radical pair originally assigned to J should be reassigned to J′ (see Figure 1). The details of the reassignment will be given elsewhere.

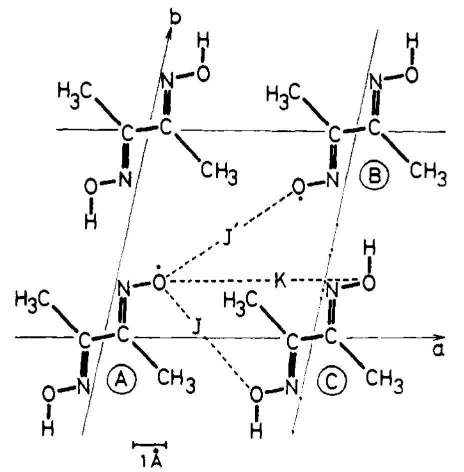

Figure 1. Projection of dimethylglyoxime molecules onto a (*ab*) plane (cf. L. Merit and E. Lantterman, *Acta Crystallogr.*, **5**, 811 (1952)). The figure indicates the specific radical pairs formed in the lattice. Pair J′ converts into pair K by the OH hydrogen atom transfer from molecule C to radical B.

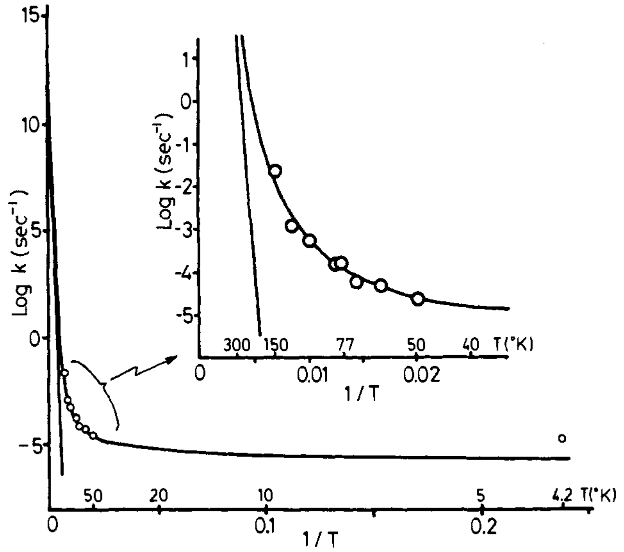

Figure 2. Arrhenius plot of the radical-pair conversion rate constants from J′ to K in the temperature range 4.2-140 K. The solid curve represents calculated tunneling reaction rate constants and the straight line indicates the classical rate constants.

Now, the conversion from J′ to K clearly indicates that hydrogen atom transfer reaction takes place between radical B and its closest neighboring molecule (C) and that the transferred proton is the OH proton. It is to be noted that, in the ESR signal of such triplet radical pairs, little changes in the zero-field splitting and its tensor axis[4] warrant that the temperature change does not cause any significant changes in the separation and the orientation of the two paired radicals in the crystalline lattice. If the hydrogen abstraction reaction of the isolated radical from the neighboring molecule is used for such studies, it is not warranted that the separation between the reactants is unchanged when the measurement temperature is altered. The hyperfine anisotropy warrants only no changes in orientation. The use of frozen solution might involve the unknown temperature change in the solvent effect. It was confirmed from the spectral details that there is no appreciable change in the lattice (considerably less than 0.5%). From these reasons, it is expected that the potential energy surface of the reaction does not change appreciably in the temperature range of our measurements.

As shown in Figure 2, the Arrhenius plot strongly bends at ~77 K and becomes nearly zero slope. However, the sharp increase in the higher temperature region indicates that the activation energy at ordinary temperature is ~10 kcal/mol or more. This means that the reaction is an ordinary hydrogen abstraction reaction by radicals in nature.[7] The solid curve is the tunneling rate constants[2c,8] calculated by the use of unsymmetrical Eckart potential and the exact solution for the permeability reported by Eckart.[9] Le Roy et al. have demonstrated that the use of the approximated formula for permeability results in serious errors especially at low temperatures.[10] The potential barriers ΔV_1 and ΔV_2 are assumed to be 15 and 16 kcal/mol, respectively (see ref 8), and the half width is taken to be 0.44 Å. The frequency factor is tentatively assumed to be 7.6×10^{12} s^{-1}. The straight line in Figure 2 is the linear relation expected from the classical reaction rate. In this calculation, we have assumed the continuous Boltzmann distribution for the translational kinetic energy of the transferred hydrogen atom.[2c] Although the agreement with the experimental points is satisfactory in the temperature range above 50 K, the slight disagreement at 4.2 K might be due to the failure of this assumption. However, the disagreement in the rate constant at 4.2 K is only a factor of 9.5. Since the classical reaction rate leads to a disagreement of a factor of 10^{764} at 4.2 K, the agreement within a factor of 10^1 is rather surprising. It should be mentioned that the rate constants (190-220 K) in DMG-d_2 reported by Lebedev et al.[5a] have been also fitted by our treatment as a result of the mass effect on tunneling.

Finally it is concluded that the tunneling process must be involved in the hydrogen atom transfer reactions. It is also suggested that the use of radical-pair conversion in single crystals is quite powerfull for the elucidation of the tunneling process in chemical reactions. One can study the reaction between two molecules which have well-defined relative orientation and dimension.

References and Notes

(1) For a review see E. F. Caldin, *Chem. Rev.*, **69**, 135 (1969).
(2) (a) E. D. Sprague and F. Williams, *J. Am. Chem. Soc.*, **93**, 787 (1971); (b) J. Wang and F. Williams, *ibid.*, **94**, 2930 (1972); (c) R. J. Le Roy, E. D. Sprague, and F. Williams, *J. Phys. Chem.*, **76**, 546 (1972); (d) G. Brunton, D. Griller, L. R. C. Barclay, and K. U. Ingold, *J. Am. Chem. Soc.*, **98**, 6803 (1976).
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(5) (a) O. Ye. Yakimchenko and Ya. S. Lebedev, *Int. J. Radiat. Phys. Chem.*, **3**, 17 (1971); (b) Ya. S. Lebedev, *Radiat. Effects*, **1**, 213 (1969).
(6) Since the half-life of the unstable radical pair is only 68 min at 77 K, the crystals were irradiated with a high dose rate (~1.4 Mrad/h) x-ray irradiator for 30 min at 77 K. Within a few minutes after irradiation, the crystals were transferred to a liquid helium Dewar.
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Kazumi Toriyama, Keichi Nunome, Machio Iwasaki*
Government Industrial Research Institute, Nagoya
Hirate, Kita, Nagoya, Japan

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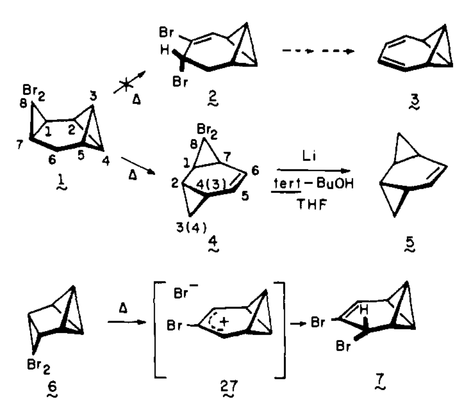
Thermal Rearrangement of Dibromotetracyclo[5.1.0.0^{2,4}.0^{3,5}]octanes. Assessment of the Competitive Opening of Dibromocyclopropane and Bicyclo[1.1.0]butane Rings and a General Synthesis of *trans*-Bishomobenzenes

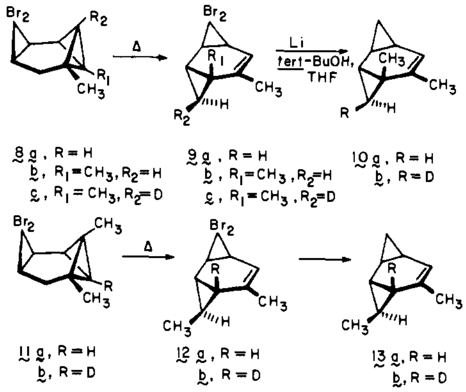
Sir:

The ready availability of tricyclo[4.1.0.0^{2,7}]hept-3-enes[1] and their established high yield conversion to dibromotetracyclo[5.1.0.0^{2,4}.0^{3,5}]octanes (e.g., **1**)[1,2] prompted us to consider the latter as possible precursors to octavalenes (e.g., **3**), highly elusive[3] conjugated dienes of considerable theoretical interest.[3c,e] Christl had previously established that thermolysis of **6** in CCl_4 (80 °C, 15 h) proceeds exclusively with dibromocyclopropane ring opening to give **7**.[4] In striking contrast, the heating of **1** and related molecules has now been found to give neither functionalized tricyclo[5.1.0.0^{2,8}]octene derivatives (**2**), nor even dibromo-*trans*-tricyclo[4.2.0.0^{2,4}]oct-7-enes,[5] but to experience unprecedented bond reorganization not involving rupture of the halogenated three-membered ring. The mechanistically revealing mapping of the carbon atom translocations to be described require total fragmentation of the bicyclobutane moiety in **1** and subsequent construction of a new cyclopropane ring through unusual transannular hydrogen shifting. Given the ease of dehalogenation of **4** and its congeners, the overall scheme is seen to comprise a heretofore unavailable general synthetic entry to variously substituted *trans*-bishomobenzenes (e.g., **10, 13, 16,** and **19**).



1 **2** **3** **4** **5** **6** **27** **7**

Gentle heating of **8a** (CCl_4, 80 °C, 8 h) resulted in smooth isomerization to **9a**.[6] This finding shows that C_5 becomes the olefinic carbon atom proximal to the unsubstituted cyclopropane ring (consult numbering schemes on **1** and **4**). Comparable treatment of a mixture of **8b** and **11a** for 4 h gave the dibromides **9b** and **12a** and ultimately hydrocarbons **10a** and **13a**. Through examination of thermal rearrangement of **8c** and **11b**, we were able to establish further in the case of **9c** (and therefore also **10b**) that the deuterium atom was positioned exo on the cyclopropyl methylene carbon. These experiments served not only to uncover the ultimate fate of the two bridgehead carbons, but also to demonstrate that stereospecific hydrogen transfer to C_3 occurs during passage to the *trans*-bishomobenzene framework. The possibility of acid evolution during these reactions was considered; however, the use of epichlorohydrin-carbon tetrachloride (1:9) or pure tetramethylethylenediamine as solvents led to identical results. Because other methyl substitution schemes required higher temperatures (see below), it appears that a C_5 CH_3 group facilitates rearrangement. A further basis of comparison is provided by **1** which requires 8 h in refluxing chlorobenzene to achieve complete isomerization to **4**.



8a, R = H
b, $R_1 = CH_3$, $R_2 = H$
c, $R_1 = CH_3$, $R_2 = D$

9a, R = H
b, $R_1 = CH_3$, $R_2 = H$
c, $R_1 = CH_3$, $R_2 = D$

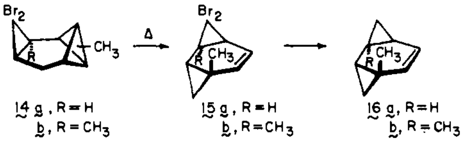
10a, R = H
b, R = D

11a, R = H
b, R = D

12a, R = H
b, R = D

13a, R = H
b, R = D

In light of the above findings, we were somewhat surprised to discover that heating of **14a** (60% syn; 40% anti) in refluxing chlorobenzene for 5 h produced a single dibromide (**15a**), characterization of which was achieved by dehalogenation to



14a, R = H
b, $R = CH_3$

15a, R = H
b, $R = CH_3$

16a, R = H
b, $R = CH_3$