

Comments on the C13 Isotope Effect in the Thermodecomposition of Ethyl Bromide

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manganese impurities in NaCl crystal, one stable at temperature above 500°C and the other stable below it. The former occurs in the quenched sample and the latter in the slowly cooled. For luminescence, the former state is much more efficient as a center.

Since both of the resonance curves do not depend upon the concentration of manganese, we may conclude that these states are some local aggregates or clusters of manganese ions and not atomic dispersions. Moreover, from the g -value and the width of the curves, it seems reasonable to suppose that the aggregates for the state in the slowly cooled sample are less dispersed.

The exact nature of these states, however, is not yet possible for us to determine. For example, the half-width of anhydrous manganese chloride is 1250 oe.¹ If the manganese ions are replacing the sodium ions to be arrayed in a (111) plane as a layer with an exchange coupling comparable to that of the anhydrous manganese chloride, the calculated value of the half-width by extreme narrowing² is 360 oe. This is larger than that for our quenched sample and much more for the slowly cooled.

The authors are much indebted to Professor S. Makishima and Professor H. Kumagai for many helpful discussions and encouragement in the course of this work.

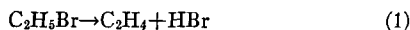
¹ Kumagai, Ôno and Hayashi, *Phys. Rev.* **85**, 925 (1952).

² P. W. Anderson and P. R. Weiss, *Revs. Modern Phys.* **25**, 269 (1953).

Mechanism of the Pyrolysis of Ethyl Bromide. A Note on a Paper by Friedman, Bernstein, and Gunning*

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(Received May 24, 1955)

THREE mechanisms¹ have been discussed in connection with the homogeneous elimination of HBr from ethyl bromide. The first is the direct unimolecular elimination

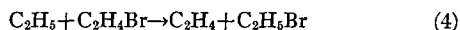
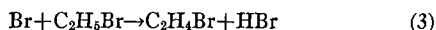
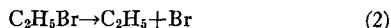


for which Blades and Murphy,² using a flow technique, and Thomas,³ using a static method have given the rate expressions

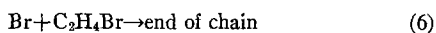
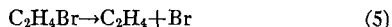
$$\log k = 12.86 - 52,300/2.303RT \quad (A)$$

$$\log k = 13.42 - 53,900/2.303RT \quad (B)$$

respectively. The second is a radical nonchain process



which may be excluded by the fact that the activation energy would be equal to the C—Br bond energy (~67 kcal).⁴ The third is a radical chain mechanism, involving steps (2) and (3) and



for which the activation energy would be less than the C—Br bond energy.

From their investigation of carbon isotope effects in the pyrolysis of ethyl bromide, Friedman, Bernstein, and Gunning¹ have concluded that the mechanism of elimination of HBr is unimolecular. These authors did not consider the possibility of the decomposition proceeding by a mixed unimolecular and radical chain mechanism, with the latter predominating. It has been shown by Daniels and Veltman that the rate constant of the uninhibited reaction in seasoned vessels is

$$\log k = 14.06 - 53,200/2.303RT. \quad (C)$$

This rate is about ten times that given by (A) and (B) and further, the uninhibited reaction differs in two important respects from

the inhibited reaction, namely the presence of induction periods and a decrease in rate constant at low pressures. It is most likely that the reaction studied by Daniels and Veltman is predominantly a radical chain reaction. Friedman *et al.* state that their rates were consistently higher than those of Daniels and Veltman, a fact which they attribute to traces of oxygen. There is no reasonable mechanism that can be adduced for oxygen catalysis of the unimolecular mechanism, so it may be concluded that the results of Friedman *et al.* refer neither to the unimolecular nor radical non-chain mechanisms, but to a radical chain mechanism in which oxygen plays a part.

The rate ratio for the radical chain reaction in the case of the pure substituted (k^*) and unsubstituted species (k) is

$$\frac{k}{k^*} = \left(\frac{k_2 k_3 k_5 k_6^*}{k_2^* k_3^* k_5^* k_6} \right)^{\frac{1}{2}}.$$

This expression will not be true for a mixture of substituted and unsubstituted ethyl bromide, since a bromine atom from $\text{C}_2^*\text{H}_5\text{Br}$ will be equally effective in initiating chains in $\text{CH}_3\text{C}^*\text{H}_2\text{Br}$, $\text{C}^*\text{H}_3\text{CH}_2\text{Br}$ and $\text{C}_2\text{H}_5\text{Br}$. It can be shown that for the radical chain reaction, Eq. (1) of Friedman *et al.* would become

$$\frac{dx_1}{dx_2} = \frac{k_3 a_0}{k_3^* a_0^* + k_3^\dagger a_0^\dagger}$$

where $a_0 = [\text{C}_2\text{H}_5\text{Br}]$, $a_0^* = [\text{CH}_3\text{C}^*\text{H}_2\text{Br}]$ and $a_0^\dagger = [\text{C}^*\text{H}_3\text{CH}_2\text{Br}]$, while k_3 , k_3^* , and k_3^\dagger are the rate constants for bromine atom attack on the above three isotopic species. If it is now assumed that $k_3^\dagger = k_3^*$, which seems reasonable, then from the experimental results at 400°C,

$$(k_3/k_3^*)_{\text{obs}} = 1.0159$$

on the assumption that the presence of oxygen only affects chain initiation.

* Friedman, Bernstein, and Gunning, *J. Chem. Phys.* **23**, 109 (1955).

¹ F. Daniels and P. Veltman, *J. Chem. Phys.* **7**, 756 (1939).

² Blades and Murphy, *J. Am. Chem. Soc.* **74**, 6219 (1952).

³ Green, Harden, Maccoll, and Thomas, *J. Chem. Phys.* **21**, 178 (1953).

⁴ Lane, Linnett, and Oswin, *Proc. Roy. Soc. (London)* **216A**, 361 (1953).

Comments on the C¹³ Isotope Effect in the Thermodecomposition of Ethyl Bromide

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(Received June 27, 1955)

RECENTLY we reported¹ data on the C¹³ isotope effect in the thermodecomposition of ethyl bromide which were thought to support the unimolecular elimination mechanism. Maccoll and Thomas² indicate that a radical chain mechanism may be used to explain the results. Preliminary experiments on the photolysis of ethyl bromide in the presence of excess cyclopentane inhibitor gave enrichments in C¹² similar to those found in the thermodecomposition, and this is probably due to a reaction similar to step (2) of reference 2. Thus the unimolecular model is apparently incorrect.

It is of interest to examine the radical chain mechanism from the viewpoint of the isotope effects. Using the symbols of reference 2, we attempt to evaluate k/k^* and k/k^\dagger . Step (2) represents $\text{C}_2\text{H}_5-\text{Br}$ dissociation, and one expects k_2 and k_2^\dagger to be very similar and both larger than k_2^* . Step (3) is quite complex and the k 's probably depend on whether the H abstraction takes place on the α or β carbon and whether C¹² or C¹³ are involved. To a first approximation all the k_3 's may be considered equal. Also, as an approximation, $k_2/k_2^* = k_6/k_6^*$. The termination step (6) may be presumed to occur primarily at the wall; here traces of oxygen could act catalytically by reducing the efficiency of chain-breaking. It is difficult to picture an isotope effect associated with this step. This reasoning leads to the conclusion that k/k^* is approximately equal to k_2/k_2^* , and that k/k^\dagger is very close to unity. Since the radical nonchain mechanism leads to the same conclusion,

this work does not seem to differentiate between the two radical mechanisms. Perhaps the use of C^{14} in each of the ethyl bromide positions would show the difference.

Since it was not very clearly stated in the first paper,¹ it should be here noted that S was calculated from the isotopic analyses using the following: [p. 111 after Eq. (6)]

$$\alpha = (C^{13}O_2)/(C^{12}O_2) \text{ from } C_2H_4$$

and

$$\alpha^0 = (C^{13}O_2)/(C^{12}O_2) \text{ from } C_2H_5Br.$$

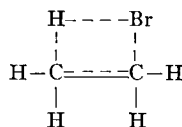
Since each molecule of labeled C_2H_4 and C_2H_5Br yields one molecule each of $C^{13}O_2$ and $C^{12}O_2$,

$$\frac{x_1}{x_2} = \frac{1-\alpha}{2\alpha} \quad \text{and} \quad \frac{a_2^0 + a_3^0}{a_1^0} = \frac{2\alpha^0}{1-\alpha^0}.$$

From the definition,

$$S = \frac{\alpha^0(1-\alpha)}{\alpha(1-\alpha^0)}.$$

The structure of the transition state shown on p. 109 is incorrectly drawn. It should be:



The results of the sample calculation on p. 111 should read:

$$S = 1.0068 \pm 0.0006; \quad \epsilon_0 = 0.0070 \pm 0.006$$

$$\frac{2k_1}{k_2 + k_3} = 1.0070 \pm 0.0006.$$

The errors range from 0.0004 to 0.0006, so the deviations in the S and S_0 headings in Table I should read $\pm 5 \times 10^{-4}$ and the small subscripts 5's should be deleted.

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¹ Friedman, Bernstein, and Gunning, *J. Chem. Phys.* **23**, 109 (1955).

² A. Maccoll and P. J. Thomas, *J. Chem. Phys.* **23**, 1722 (1955).

Thermochromism and Photochromism

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(Received December 23, 1954)

THE phenomenon of reversible formation of colored modifications of compounds related to dianthrone by ultraviolet irradiation at low temperatures was first reported by Y. Hirshberg in 1950¹ and named photochromism.

In subsequent publications from this laboratory details about this phenomenon and its relation to thermochromism were reported both in the dianthrone series² and in the spiran series.^{3,4}

It was concluded from these investigations that the dyes which were reversibly formed both in thermochromism and in photochromism were identical.

In a recent publication⁵ Kortum, Theilacker, and Braun, ignoring the facts mentioned in the beginning of this letter, challenged our above conclusion on the basis that the ultraviolet absorption spectrum of the thermochromic dye B is similar to that of the colorless modification A , whereas the absorption of the photochromic dye C differs from that of A .

These authors thus seem to have disregarded the basic fact elaborated in our above publications that in thermochromism, as distinct from photochromism, only a small and difficultly assessable fraction (generally between 0.1 and 5%) of A is thermally converted into the dye modification. The observed absorption spectrum, therefore, results from the superposition of the spectra of the dye B and a large excess of A , in equilibrium with B . Under such conditions it is practically impossible to estimate with any

degree of accuracy the absorption of B in the ultraviolet region, in which A also absorbs. The spectra of B and C can therefore be compared only within the visible region where the excess of A , which accompanies B , does not interfere. Our results clearly show that in this region B and C are indeed identical, apart from changes resulting from the difference in temperatures of measurements (above 100° in thermochromism and below -100° in photochromism).

We wish to point out that Kortum, Theilacker, and Braun's claim in their paper⁵ that form C presents absorption bands in the visible region which are not present in form B is based on consideration of a compound which is photochromic and *non-thermochromic*, so that comparison of the spectra of the two forms is obviously impossible. The presumed extra "photochromic" bands appearing in Fig. 3 of the above paper are already recognizable in the curve (same figure) given for irradiation (time not reported) at 20°C, at which temperature form C does not exist. Accentuation of these bands on irradiation (50 minutes) at -115°C may well be due to some photochemical decomposition; no similar bands appear in the case of 1,2,7,8'-dibenzbianthrone (Fig. 5) (also photochromic only), presumably on account of its greater photochemical stability.

The existence of bianthrone derivatives, which are photochromic and nonthermochromic, may be explained by the following.

Thermochromism represents a thermal equilibrium, the position of which depends on the energy difference between the two modifications A and B . It is, therefore, plausible that for derivatives of dianthrone, which show only photochromism and not thermochromism, this energy difference is so large that no observable shift of the equilibrium towards the colored species occurs within the accessible temperature range.

Note added by Y. Hirshberg:—I infer from Kortum and Theilacker's reply below that they must have been misled by inadequate knowledge of the French language. In fact, the paper¹ referred to in their reply, and from which a passage is quoted, deals with thermochromism and has nothing to do with photochromism. As to the subsequent arguments of these authors, these are untenable in view of our above Letter to the Editor.

¹ Y. Hirshberg, *Compt. rend.* **231**, 903 (1950).

² Y. Hirshberg and E. Fischer, *J. Chem. Soc.* 629 (1953).

³ Y. Hirshberg and E. Fischer, *J. Chem. Soc.* 4522 (1952); 2184 (1953); 297, 3129 (1954).

⁴ Y. Hirshberg and E. Fischer, *J. Chem. Phys.* **21**, 1619 (1953).

⁵ Kortum, Theilacker, and Braun, *Z. physik. Chem. N.F.* **2**, 179 (1954).

Thermochromism and Photochromism

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(Received January 17, 1955)

THE discovery of the "photochromism" of dehydrodianthrone—as opposed to the "thermochromism" of the same compound—by Bergmann and co-workers¹ has already been quoted by us in a previous paper.² Unfortunately a reference to the earlier contribution by Hirshberg³ was not given in that publication¹ so that we missed it. We are grateful for this having been called to our attention.

The identity of the thermochromic form B and of the photochromic form C of the dehydrodianthrone has been considered as very improbable by Hirshberg himself in the above quoted paper¹ "Il paraît probable que la thermochromie à haute et à basse température n'est pas due au même type d'excitation électronique," and reasons for this opinion are discussed. Our measurements also argue against the identity of forms B and C . The possibility of detecting a small contribution of the thermochromic form B in the presence of an excess of the form A of the compound and also in the uv where the absorptions are overlapping, depends firstly on the differences in position and in-