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Letters to the Editor

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An Attempt to Find Cross Products in the Benzidine Rearrangement

G. W. WHELAND AND J. R. SCHWARTZ*

Department of Chemistry, University of Chicago, Chicago, Illinois
February 25, 1949

SINCE cross-products have never been observed in the benzidine rearrangement, the reaction is considered to be purely intramolecular. One may, however, doubt whether the methods employed heretofore in the search for cross-products have been sensitive enough to detect the presence of small amounts of these substances. We have accordingly studied the problem with the use of C^{14} as a radioactive tracer.

The most reliable method for determining whether cross-products are formed in the benzidine rearrangement is doubtless that of Ingold and Kidd,¹ in which a mixture of two symmetrical hydrazobenzenes is rearranged. Although we have not yet solved all the problems connected with the practical application of this method, we have obtained some preliminary results for the rearrangement of an unsymmetrical hydrazobenzene. 2-Methyl-2'-ethoxyhydrazobenzene, with C^{14} in the methyl group, was rearranged in absolute ether by the addition of the calculated amount of alcoholic hydrogen chloride. To the resulting precipitate was then added an approximately equivalent quantity of non-radioactive *o*-tolidine dihydrochloride, a possible cross-product. The mixture was transformed into a mixture of Schiff's bases by refluxing with benzaldehyde and potassium acetate in absolute ethanol. The resulting dibenzal-*o*-tolidine, being practically insoluble in ethanol, remained undissolved. This material, after two crystallizations from benzene, had a residual radioactivity only 0.2–0.5 percent as great as would have been expected if the original rearrangement had produced *only* the two cross products, *o*-tolidine and 3,3'-diethoxybenzidine. This residual activity was still decreasing when the smallness of the remaining sample required the purification to be discontinued; hence, a completely inactive material might ultimately have been obtained. In any event, the cross-product clearly amounts to much less than one percent of the total product of the rearrangement.

Materials. Benzoic acid² was reduced to benzyl alcohol with lithium aluminum hydride,³ and then to toluene with hydrogen and palladium on charcoal. The toluene was nitrated in acetic anhydride, and the isomeric nitrotoluenes were separated by distillation. The *o*-nitrotoluene was then transformed into *o*-nitrosotoluene, which was condensed with *o*-phenetidine in ligroin containing a little glacial acetic acid. The resulting 2-methyl-2'-ethoxyhydrazobenzene melted at 70–71°C. Anal. Calcd. for $C_{15}H_{16}N_2O$: N, 11.68. Found: N, 11.31. Reduction with hydrogen sulfide in alcoholic ammonia gave the hydrazo compound, melting at 95–97°C. Anal. Calcd. for $C_{15}H_{18}N_2O$: N, 11.58. Found: N, 11.4. Dibenzal-*o*-tolidine melted at 157–158°C. Anal. Calcd. for $C_{28}H_{24}N_2$: N, 7.22. Found: N, 7.13.

Radiochemical technique. The standard procedures, as described by Kamen⁴ and by Libby,⁵ were employed. The counter used was of the end-window type.

The authors gratefully acknowledge much help with the radiochemical measurements from Professor W. F. Libby and Mr. E. C. Anderson.

* Present address, Department of Chemistry, University of California at Los Angeles, Los Angeles, California.

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Isotope Effect in the Decarboxylation of Labelled Malonic Acids

JACOB BIGEISEN

Brookhaven National Laboratory, Upton, Long Island, New York
January 28, 1949

RECENTLY Yankwich and Calvin^{1,2} have synthesized and decarboxylated malonic and brom-malonic acids with tracer C^{14} in the carboxyl group. They find that the specific activity of the carbon dioxide formed in the decarboxylation is significantly different from that calculate on the assumption that the rate constant for the evolution of $C^{14}O_2$ is one-half that of $C^{12}O_2$ in the normal acids. Their results are reported as the relative probabilities of rupture of $C^{12}-C^{12}$ bonds as compared with $C^{12}-C^{14}$ bonds. They find for malonic acid at 150°C $C^{12}-C^{12}/C^{12}-C^{14} = 1.12 \pm 0.03$ and for brom-malonic acid at 115°C $C^{12}-C^{12}/C^{12}-C^{14} = 1.41 \pm 0.08$.

It has been estimated³ that an upper limit for the ratio of rates for a compound containing C^{12} compared with one containing C^{14} is 1.5 at 298°K, apart from a factor arising from symmetry numbers. The deviation of the ratio from unity decreases rapidly with increasing temperature and this estimated upper limit becomes 1.35 at 400°K. This estimate is made for reactions which proceed through monatomic carbon gas (chemically improbable at these temperatures) as the activated complex. In view of the fact that the results reported by Yankwich and Calvin approach this upper limit so closely even after decarboxylation of *all* of the substrate, it seems worth while to consider the reaction in a little detail from a theoretical viewpoint.

Kinetically the reaction is very simple and has been shown to be first order for malonic acid both in glacial acetic acid⁴ and in the pure liquid.^{5,6} A summary of the kinetic data on the molten malonic acid is given in Fig. 1. The point marked S is for supercooled liquid. After correcting the entropy of activation (calculated assuming unity for the transmission

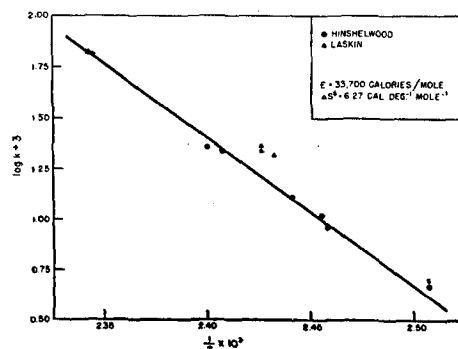


FIG. 1. Decomposition of malonic acid.

TABLE I.

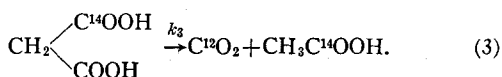
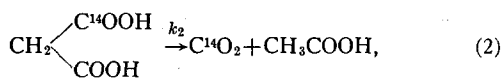
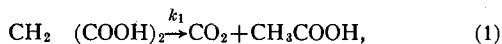
Brom-malonic acid			Malonic acid		
ω	$\Delta\omega$		ω	$\Delta\omega$	ω (Infra-red, see reference 8)
ω_1	458	7.1	756	2.4	765
ω_2	196	3.3	230	4.4	
ω_3	505	6.6	905	3.6	894

TABLE II. Calculated isotope effect in the decarboxylation of malonic acids.

$T^\circ\text{K}$	Brom-malonic acid		Malonic acid	
	$k_1/2k_2$	$k_1/2k_3$	$k_1/2k_2$	$k_1/2k_3$
300	1.044	1.0063	1.042	1.0041
350	1.043	1.0048		
385	1.042	1.0040		
400	1.042	1.0037	1.041	1.0029
425	1.041	1.0033	1.041	1.0026
500			1.040	1.0019

coefficient) for the destruction of symmetry in the activated complex ($R1n2$) we find the activated complex 4.9 e.u. higher than the liquid. There is no evidence of any type of chain reactions.

The specific activity of the CO_2 formed at any time can be calculated in terms of the initial specific activity and the rate constants defined by the following equations:



The initial numbers of moles of ordinary and labeled malonic acids are defined as Mo^{12} and Mo^{14} , respectively. Then

$$\frac{\text{C}^{12}\text{O}_2}{\text{C}^{14}\text{O}_2} = \frac{\text{Mo}^{12}(1 - e^{-(k_2+k_3)t})}{\text{Mo}^{14}(1 - e^{-(k_2+k_3)t})k_2}.$$

For t small,

$$\frac{\text{C}^{12}\text{O}_2}{\text{C}^{14}\text{O}_2} = \frac{\text{Mo}^{12}k_1}{\text{Mo}^{14}k_2};$$

at $t = \infty$,

$$\frac{\text{C}^{12}\text{O}_2}{\text{C}^{14}\text{O}_2} = \frac{\text{Mo}^{12}k_2 + k_3}{\text{Mo}^{14}k_2}.$$

We shall estimate the ratios $k_1/2k_2$ and $k_1/2k_3$ by the method⁷ previously applied to the calculation of the isotope effect in the rupture of C—C bonds in propane — $1-\text{C}^{13}$. This model should give an upper limit to the ratios and in addition predicts that the entropy of activation will be positive.

The force constants for the skeletal vibrations are chosen⁸ as $k_{\text{C-C}} = 4.1 \times 10^5$ dynes/cm and $k_{\text{C-H}} = 0.35 \times 10^6$ dynes/cm. The calculated and found frequencies⁸ are given in Table I. The ratio $(k_2 + k_3)/k_2$ depends upon the masses of the carbon atoms alone⁷ and equals 2.0378 for both acids. The calculated ratios for $k_1/2k_2$ and $k_1/2k_3$ are given in Table II.

The disagreement between theory and experiment is independent of the model of the activated complex chosen since the reciprocal of the specific activity of CO_2 at complete decarboxylation is proportional to $(k_2 + k_3)/k_2$, which is a function of the masses in the normal molecules alone.

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Ultraviolet Absorption by Hydrogen-Bridged Molecules*

GLADYS A. ANSLOW, HSI-TEH HSIEH, AND RUTH C. SHEA
Department of Physics, Smith College, Northampton, Massachusetts
January 27, 1949

THE short wave-length continua appearing in the 220–190 μ region in the spectra of fatty and amino acids have been ascribed by the senior author¹ to the dissociation of hydrogen bridged bonds in the respective associated molecules, the absorbed photon energy being dissipated according to the equation

$$E_{\text{photon}} = E_e(\text{OH})^* + D_v'(\text{OH}) + D_v'(\text{H} \cdots \text{O}),$$

where $E_e(\text{OH})^*$ is the electronic energy of the excited state, i.e., of the (O,O) transition, 4.02 eV (32410 cm^{-1}) for the 3064A OH band in water vapor, and $D_v'(\text{OH})$ and $D_v'(\text{H} \cdots \text{O})$ are the excited state vibrational energies of the bond and the bridge, which are equivalent as a result of the resonating structure.

The dissociation energy of a polyatomic molecule is determined by the vibration frequencies and anharmonicity constants which appear in infra-red stretching vibrations.² Consequently, the energies required to dissociate molecules with similar electronic configurations in the vibrating bonds must vary approximately as $D_v'(1)/D_v'(2) = \{\mu_2/\mu_1\}$, where μ_1 and μ_2 are the reduced masses of the respective molecules. Consequently the dissociation energies of the bonds and the bridges in $\text{OH} \cdots \text{O}$ polymers may be calculated from the dissociation energy of water vapor in the excited state, approximately 2.4 eV³ and the respective reduced masses of the corresponding molecules. Such calculations indicate dissociation energies which agree within one percent with the energies indicated by the long wave-length edges of the ultraviolet continua reported by the senior author and others⁴ for glycine, alanine, butyric acid, cysteine, phenylalanine, and tryptophane, and within three percent with the energies indicated by the continua in the spectra of aspartic acid, succinic acid, glutamic acid and tyrosine.

A search for $\text{OH} \cdots \text{O}$ dissociation bands in the spectra of the heavy alcohols and the starches and for $\text{NH} \cdots \text{O}$ dissociation bonds in the spectra of the amides and related molecules has resulted in the identification of such bands and also of three weaker absorption bands; the (O,O) electronic excitation with center near 32400 cm^{-1} , the D'' vibrational dissociation of the OH or the NH unassociated bonds, and the $\text{OH} \cdots \text{O}$ or the $\text{NH} \cdots \text{O}$ dissociation of hydrogen bridged bonds in the unexcited state. These are easily identified in the spectra of the alcohols, shown for amyl alcohol in Fig. 1. Relative values of the maximum extinction coefficients of the two vibration bands indicate the degree of association. The long wave-length edges indicate OH bond energies in the lighter alcohols of 4.47–4.49 eV, approximately the 4.46-eV value calculated for the OH bond energy in water by Gaydon⁵ or the 4.36-eV value calculated by Dwyer and Oldenberg.⁶ The energy of the hydrogen bridge in the unexcited state, $D_v''(\text{OH} \cdots \text{O}) - D_v''(\text{OH})$, is approximately 0.31 eV per molecule, (7.1 kcal./mol).

Similarly values of the electronic energy for the (O,O) band, and of vibrational energies of the NH bond in unassociated and associated molecules, as well as the energy required to dissociate both the NH bond and the $\text{H} \cdots \text{O}$ bridge in the excited state have been calculated from bands appearing in the absorption spectra of urea, acetamide, propionamide, butyramide, allantoin, and hydantoin solutions. Some of these specimens had been heat treated to produce different types of association.⁸ A typical spectrum for propionamide is shown in part 2 of the figure. The average value of $D_v''(\text{NH})$ given by these spectra is 3.71 eV, very close to the thermodynamically calculated value 3.74 eV given by Glockler.⁷ The onset of absorption near 32000–33000 cm^{-1} may be ascribed