Ultraviolet Absorption by HydrogenBridged Molecules

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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.

| | Brom-malonic acid | | Malonic acid | |
$T°K$	$k_1/2k_2$	$k_1/2k_3$	$k_1/2k_2$	$k_1/2k_3$
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:

$$CH_2\ (COOH)_2 \xrightarrow{k_1} CO_2 + CH_3COOH, \tag{1}$$

$$CH_2 \begin{array}{c} C^{14}OOH \\ \diagup \\ \diagdown \\ COOH \end{array} \xrightarrow{k_2} C^{14}O_2 + CH_3COOH, \tag{2}$$

$$CH_2 \begin{array}{c} C^{14}OOH \\ \diagup \\ \diagdown \\ COOH \end{array} \xrightarrow{k_3} C^{12}O_2 + CH_3C^{14}OOH. \tag{3}$$
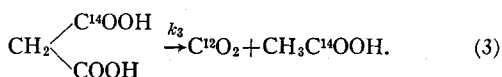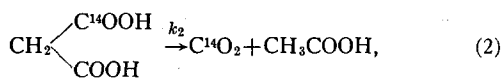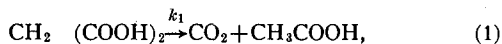
The initial numbers of moles of ordinary and labeled malonic acids are defined as Mo^{12} and Mo^{14}, respectively. Then

$$\frac{C^{12}O_2}{C^{14}O_2} = \frac{Mo^{12}(1-e^{-k_1\,t})(k_2+k_3)}{Mo^{14}(1-e-(k_2+k_3)t)k_2}.$$

For t small,

$$\frac{C^{12}O_2}{C^{14}O_2} = \frac{Mo^{12}k_1}{Mo^{14}k_2};$$

at $t = \infty$,

$$\frac{C^{12}O_2}{C^{14}O_2} = \frac{Mo^{12}}{Mo^{14}}\frac{k_2+k_3}{k_2}.$$

We shall estimate the ratios $k_1/2k_2$ and $k_1/2k_3$ by the method[7] previously applied to the calculation of the isotope effect in the rupture of $C-C$ bonds in propane $-1-C^{13}$. 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 chosen[8] as $k_{C-C} = 4.1 \times 10^5$ dynes/cm and $k\delta = 0.35 \times 10^5$ dynes/cm. The calculated and found frequencies[8] are given in Table I. The ratio $(k_2+k_3)/k_2$ depends upon the masses of the carbon atoms alone[7] 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*

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January 27, 1949

THE short wave-length continua appearing in the 220–190 mμ region in the spectra of fatty and amino acids have been ascribed by the senior author[1] to the dissociation of hydrogen bridged bonds in the respective associated molecules, the absorbed photon energy being dissipated according to the equation

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

where $E_e(OH)^*$ 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 $D_v'(OH)$ and $D_v'(H\cdots O)$ 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 OH$\cdots$O polymers may be calculated from the dissociation energy of water vapor in the excited state, approximately 2.4 ev[3] 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 others[4] 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 OH$\cdots$O dissociation bands in the spectra of the heavy alcohols and the starches and for NH$\cdots$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 OH$\cdots$O or the NH$\cdots$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 Gaydon[3] or the 4.36-ev value calculated by Dwyer and Oldenberg.[5] The energy of the hydrogen bridge in the unexcited state, $D_v''(OH\cdots O) - D_v''(OH)$, 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 H$\cdots$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.[6] A typical spectrum for propionamide is shown in part 2 of the figure. The average value of $D_v''(NH)$ 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
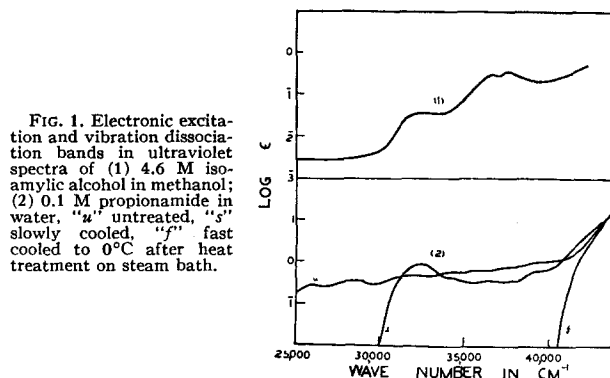
FIG. 1. Electronic excitation and vibration dissociation bands in ultraviolet spectra of (1) 4.6 M isoamylic alcohol in methanol; (2) 0.1 M propionamide in water, "*u*" untreated, "*s*" slowly cooled, "*f*" fast cooled to 0°C after heat treatment on steam bath.

to $D_v''(NH\cdots O)$ and indicates that the strength of the hydrogen bridge in these molecules is approximately 0.25–0.30 ev (5.7–6.9 kcal./mol). The wave numbers ascribed to the (O,O) electronic transition run between 29400 and 29000 cm^{-1}, close to the 29750 cm^{-1} value observed for the origin of this absorption band in the emission spectrum of nitrogen hydride. The strong absorption continua appearing between 230–260 mμ in these spectra must result from the dissociation of hydrogen-bridged bonds in the respective dimers or trimers.

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Thermal Conductivity of Gases and Aggregate Matter

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February 10, 1949

THE production of more data on the conductivity of gases has recently been considered to be of major importance.[1] It appears to the writer that since the direct determination of thermal conductivities of gases at high temperatures is practically impossible (due to the magnitude of radiation corrections, etc.), the need may be met in two other ways. One is from computation as the theory of gases is extended, the other is from thermal conductivity measurements of powdered or aggregate matter. This note gives some preliminary results as obtained in the study of heat flow in aggregates now under way in these laboratories, together with some data from the literature, and a few calculated values for zero pressure gases, using the Eucken assumption.

Our data[2] for a fused magnesia powder of 51.5 percent porosity may be expressed by

$$k(\text{c.g.s.}) = 6.2 \times 10^{-4}(1 + 0.843 \times 10^{-3} t°C).$$

The data of Borelius and Wilner[3] for a magnesia powder of apparent density 0.456 (87.2 percent porosity with $d_0 = 3.57$) may be expressed by $k = 2.205 \times 10^{-4}(1 + 0.8057 \times 10^{-3} t)$.

The three points of Pierce and Austin[4] for a finely divided (precipitated) calcined magnesia, porosity not known, may be expressed reasonably well by $k = 1.7 \times 10^{-4}(1 + 2.3 \times 10^{-3} t)$. The writer's computed values for air may be expressed approximately for comparison by

$$k = 0.585 \times 10^{-4}(1 + 2.15 \times 10^{-3} t).$$

The data of Knapp[5] for a single crystal of synthetic periclase may be expressed approximately as

$$k = 111 \times 10^{-4}(1 + 2.117 \times 10^{-3} t) \quad \text{to} \quad 499°C.$$

Borelius and Wilner[3] also have data on pure kieselguhr ($d = 0.267$; for $d_0 = 2.65$, porosity is 90 percent). For comparison

$$k = 1.175 \times 10^{-4}(1 + 1.5^{-7} \times 10^{-3} t)(0-600°C).$$

All of the above were at atmospheric pressure. With accumulation of more data on aggregates, it therefore seems that the proper functions may be deduced to permit extrapolation to 100 percent porosity, thus giving the thermal conductivity of the gas (see Fig. 1). Too high porosities of aggregate evidently should not be employed for experimentation (danger of radiation and convection effects).

Obviously determinations on the same aggregate with different gases present would seem to offer a means of obtaining relative conductivities. However, the proper treatment of data is by no means clear as yet. Budrin and Golubev[6] report increases, on replacing nitrogen with hydrogen, of 1.7 and 2.9 times for vermiculite and diatomite powders at 700°C and 0°C, respectively, less for diatomite bricks. Unfortunately, this paper could not be obtained for study. From our calculated values for gases, $k\text{H}_2/k\text{N}_2$ at 700° is 0.945 times that (6.987) at 0°C. Hence the effect is not as large as would be anticipated. It may well be that the light gases, helium and hydrogen, behave abnormally in conduction, a behavior which may be indicated by their accommodation coefficients at much lower temperatures. One may also cite the results of Kannuluik and Martin[7] with a very low density magnesia powder ($d = 0.20$, porosity with $d_0 = 3.57$, 94.5 percent). At 757 mm Hg, k in air was 17.5×10^{-5}, in hydrogen 46.6×10^{-5} and 762 mm Hg (both probably near 0°C). The ratio here was 2.66, while the ratio $k\text{H}_2/k$ air at 0°C is 7 (data of Johnston et al.[8]). The accommodation coefficients (a') on bright platinum given by Johnston et al.[9] are for hydrogen, 0.40; for air 0.75 (at 279–80°K).

The writer obtained k in He/k in air at 700°C = 1.24[8] but this probably was due to incomplete replacement of air by helium, due to the design of the first unit.
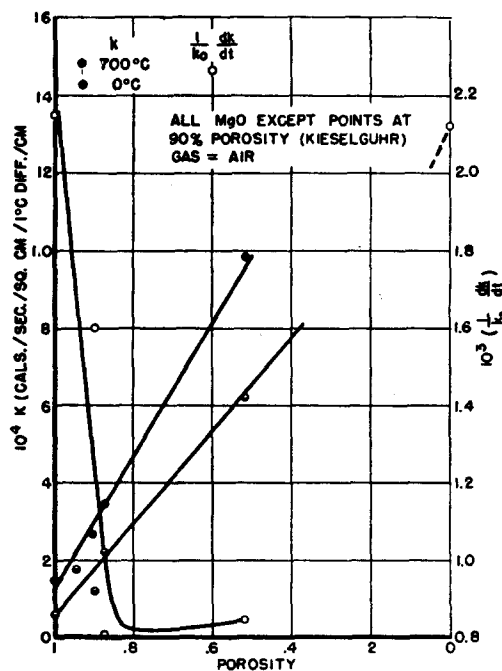

FIG. 1. Thermal conductivity *versus* porosity for various materials.