Photodissociation of Polyatomic Molecules in the Schumann Ultraviolet

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Concerning Hydrocarbon Bond Additivity

The data of Kistiakowsky, Ruhoff, Smith and Vaughan[1] on the heats of hydrogenation of some olefins furnish a test for the corrections proposed by the author[2] to obtain bond additivity. The two corrections proposed were (1) inclusion of the zero-point vibrational energy of each molecule in its total potential energy; (2) an additional interaction between those hydrogen atoms attached to the same carbon atom. The latter is admittedly, at present, an empirical correction factor.

Consider the reaction involved in hydrogenation; namely, $C_nH_{2n}+H_2 \rightarrow C_nH_{2n}+2$. The sum total effect is to dissociate 1 C=C bond and one molecule of H_2, and to form 1 C−C and 2 C−H bonds. But, in addition, two further changes occur; first, the sum of the zero-point energies of the reactants differs from that of the product. Second, the H···H interaction is greater in the saturated hydrocarbon and, in addition, depends specifically on the position of the double bond in the olefin. For example, ethylene has 2 H···H interactions, ethane has 6, the change amounting to 12 Kcal.; propylene has 4 H···H, propane has 7, the change amounting to 9 Kcal.; butene (2) has 6 H···H, normal butane has 8, the change being 6 Kcal.

In general, then, the heat of hydrogenation of C_nH_{2n} may be written as follows:

$$\Delta H = \{H_{C-C}+H_{2C-H}+H_\delta(_{H...H})+\epsilon_{C_nH_{2n+2}}\} \\ -\{H_{C-C}+109.3+\epsilon_{C_nH_{2n}}\} \cdots (1)$$

where H_{C-C}, H_{C-H}, H_{C-C} are the bond strengths of the bonds noted in subscript; $H_{\delta H...H}$ is the change in the H···H interaction which is realized on hydrogenation; ϵ denotes the zero point energy; 109.3 Kcal. is the heat of dissociation of H_2 plus its vibrational zero-point energy.

The zero-point energies of the saturated hydrocarbons are obtained from the frequency date of Kohlrausch and Köppel.[3] The frequencies for ethylene were taken from the analysis of Mecke.[4] No Raman nor infrared data are available at present from which one may estimate the frequencies for propene and the butenes. However, data do exist for the aldehydes and the ketones,[5] which furnish the means for a comparison. The skeleton vibrations in propene are approximated by acetaldehyde; those in butene (1) by propylaldehyde; those in isobutene ,by acetone. From analogy with the *cis* and *trans* modifications of dichlorethylene, butene (2, *cis*) should have a frequency distribution more like isobutene, while butene (2, *trans*) is more like the chain found in butene (1). Since we are expressing energies in kilocalories, this estimation is not very sensitive to the value of the frequency chosen, provided the total number of vibrational degrees of freedom are satisfied. For example, the stretching vibrations of the hydrogens alone contribute a little more than half the zero-point energy. Since the number of degrees of freedom for the stretching frequencies of C−H bonds equals the number of hydrogen atoms, and since these frequencies are all in the region 2800 to 3000 wave numbers, only a very small uncertainty is entailed if the assignment is in error.

Using the values for the C−H bond and the H···H interaction from reference 2, and the observed heat of hydrogenation for ethylene the C=C bond was obtained of 138.5 Kcal. The remaining heats of hydrogenation were then calculated as given in Table I.

TABLE I.

	$H_{\delta H \cdots H}$	$\epsilon_{C_nH_{2n}}$	$\epsilon_{C_nH_{2n+2}}$	ΔH (Calc.)	$\Delta H(0°K)$ (Obs.)
Ethylene	12	33.4	44.2	――――	31.0
Propylene	9	50.5	61.7	28.4	28.3
Butene (1)	9	67.0	78.4	28.6	28.5
Isobutene	6	66.0	78.6	26.8	26.6
Butene (2, *cis*)	6	66.0	78.4	26.6	26.8
Butene (2, *trans*)	6	67.0	78.4	25.6	25.8

The value of 138.6 for the C=C bond is higher than that calculated from the heat of combustion data, but is more probable because of the uncertainties in the combustion data for ethylene. The use of this value for the C=C bond does not change the conclusions arrived at in the first communication of the author.[2]

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[1] Kistiakowsky, Romeyn, Smith and Vaughan, J. Am. Chem. Soc. 57, 65 (1935); Kistiakowsky, Romeyn, Smith and Vaughan, J. Am. Chem. Soc. 57, 876 (1935).
[2] V. Deitz, J. Chem. Phys. 3, 58 (1935).
[3] Kohlrausch and Koppel, Zeits. f. physik. Chemie B26, 209 (1934).
[4] Mecke, Zeits. f. Physik 64, 173 (1930).
[5] Kohlrausch and Köppel, Zeits. f. physik. Chemie B24, 370 (1933).

Photodissociation of Polyatomic Molecules in the Schumann Ultraviolet

Very valuable information concerning the way a molecule is disrupted on absorption of light may be obtained from the absorption spectrum; the interpretation is, however, seldom definite, especially in the case of broad continuous regions of absorption exhibited, as a rule, by polyatomic molecules.

A direct observation of the photodissociation process becomes possible when the magnitude of the absorbed quantum is large enough to disrupt a molecule into *excited* radicals which can be then detected by their emission. From the study of this emission various important details regarding the mechanism of the disruption can be obtained, as was shown in a series of papers from this laboratory.[1]

For the extension of this method to polyatomic organic molecules, radiation in the Schumann ultraviolet must be used, since large energies are required to disrupt bonds in these molecules with simultaneous excitation of the radicals set free.

During some researches on gaseous photochemical reactions in the Schumann ultraviolet,[2] we observed that in the vapors of H_2O, CH_3OH and CH_3CN, the bands belonging to OH and CN radicals are emitted under the action of this short radiation.[3]

The work has been lately extended to organic acids,

ammonia and methylamine. In all these experiments the vapor of the substance studied was subjected to intense illumination through a thin fluorite window from a powerful hydrogen discharge tube, or a spark in an argon atmosphere. The shortest acting wavelength was 1300A. By interposing a thin film of fused quartz, wavelengths shorter than 1500A could be easily cut out and the range of active wavelengths thus approximately determined. In nearly all cases the observed emission disappeared when the quartz film was inserted in the path of the exciting light.

The results so far obtained are summarized in the following table, where under $D+E$ are given the threshold energies needed to produce the dissociation process represented in the preceding column; the wavelengths corresponding to these energies are given in Table I under λ_0.

TABLE I.

Substance:	Process:	$D+E$ (kcal.)	λ_0 (A)
H_2O	$H+OH^*$	$115+92=207$	1400
CH_3OH	CH_3+OH^*	$90+92=182$	1560
C_2H_5OH	$C_2H_5+OH^*$	$90+92=182$	1560
$HCOOH$	$HCO+OH^*$	$90+92=182$	1560
CH_3COOH	CH_3CO+OH^*	$90+92=182$	1560
CH_3CN	CH_3+CN^*	$105+73=178$	1600
NH_3	$H+NH_2^*$	$117+55=172$	1650
I_2	$I+I^*$	$35+159=194$	1460

The hydroxyl radicals were detected by the emission of the known band 3062A (92 kcal.), the cyanogen radical by the characteristic bands beginning with the 3883A (73 kcal.) one. In ammonia and methyl amine vapors a visible emission appears under the action of Schumann radiation, consisting of a broad band lying in the green-yellow part of the spectrum (probably α-bands of ammonia). This emission which is now being studied with larger dispersion, presumably belongs to an excited NH_2 radical liberated from the ammonia molecule in the dissociation process represented above.

Under the action of these short wavelengths iodine vapor emits the atomic line 2062A of iodine. This points to a photodissociation of the iodine molecule with the excitation of one of the iodine atoms to the $6s\ ^2P_{3/2}$ state, from which the emission of this line occurs.

The direct observation of free radicals with the help of their emission opens the way to a spectral study of the kinetics of various reactions they can undergo in collisions with other molecules. We are therefore studying now the quenching of this emission, as well as the efficiency of vibration energy transfers from these excited radicals to various other molecules. A full account of the whole work will be given at another place.

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[1] A. Terenin, Zeits f. Physik **44**, 713 (1927); cf. also; Physik. Zeits. d. Sowjetunion **2**, Heft 4–5 (1932); A. Terenin, Nature **135**, 543 (1935); Comptes rendus Acad. Leningrad, 1935, 485.
[2] H. Neujmin and B. Popov, Zeits. f. physik. Chemie **B27**, 15 (1934); see also forthcoming paper of B. Popov in Acta phys. chim. URSS on the reaction $O'+CO$.
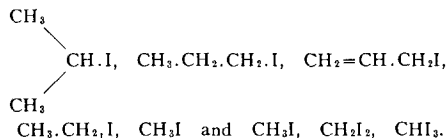[3] A. Terenin and H. Neujmin, Nature **134**, 255 (1934).

Isotopic Exchange Reactions with Iodine

The reaction $RX+I^-=RI+X^-$ ($R=$ organic radical, $X=$ Cl, Br, I) has been the subject of several well-known investigations.[1] When $X=I$ the only possibility of observing the reaction has been to make R an optically active radical, and to follow the racemization occurring in the reaction. This prevents the use of the method in the case of the simple alkyl radicals (besides involving an assumption concerning the connection between the racemization and the reaction mechanism). The use of the radioactive iodine isotope provides a method free from any theoretical assumption and of general applicability. Using a Geiger-Müller counter, we have observed some of these isotopic exchange reactions.

Sodium iodide and iodine were activated in sealed tubes sunk in a paraffin block by bombardment with neutrons from a source of 100 millicuries of radon sealed up with beryllium powder.

We will not consider here the effect of momentum of the neutron absorbed by the iodine nucleus and of the gamma-ray emitted, upon the form (ion, atom or molecule) in which the radio-iodine is obtained when Na^+I^- or I_2 are activated, because the question is complex. But on the strength of the two following results we conclude that when activated (solid) Na^+I^- is dissolved in water, the solution contains the radio-iodine in the form of RI^- ions. Activated Na^+I^- was dissolved in water, and inactive iodine added. On extracting the iodine by CS_2 the activity was found to be divided between the iodide and the iodine. Similarly, starting with activated iodine and inactive Na^+I^- the activity was shared.

We have examined two series of aliphatic iodine compounds:

$$CH_3 \diagdown$$
$$CH.I, \quad CH_3.CH_2.CH_2.I, \quad CH_2=CH.CH_2I,$$
$$CH_3 \diagup$$

$$CH_3.CH_2.I, \quad CH_3I \quad \text{and} \quad CH_3I,\ CH_2I_2,\ CHI_3.$$

The procedure for the exchange experiments was dictated by the short half-life period of radio-iodine (*ca.* 24 minutes). Activated sodium iodide was dissolved (*ca.* $\frac{1}{2}N$) in alcohol with a few percent of water. To this solution the alkyl iodide (*ca.* 2N) was added. After about 1 minute the organic iodide was precipitated by excess water, separated from the water layer and repeatedly washed. For the counter measurements AgI was prepared from both the organic iodide and the NaI solution by adding respectively alcoholic or aqueous silver nitrate. In the case of methylene iodide the iodine was first liberated by boiling with concentrated sulphuric acid. The iodoform was dissolved in acetone (containing the activated NaI) and after precipitation tested directly.

With CH_3I and $CH_2=CH.CH_2I$, in one minute at room temperature and under the conditions of solvent and concentration stated, the exchange took place to a considerable extent (>50 percent). With the other substances the exchange was negligible or small (certainly less than 10 percent).