Isotopic Exchange Reactions with Iodine

F. Juliusburger, B. Topley, and J. Weiss

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.

A. TERENIN
H. NEUJMIN

Photochemical Laboratory of the Optical Institute,
    Leningrad 53, USSR,
    May 25, 1935.

[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.
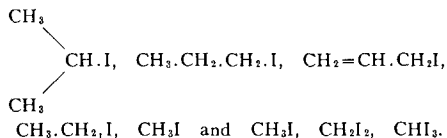[3] A. Terenin and H. Neujmin, Nature **134**, 255 (1934).

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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:

$$CH_3{\diagdown\atop\diagup}CH.I, \quad CH_3.CH_2.CH_2.I, \quad CH_2=CH.CH_2I,$$
$$CH_3$$
$$CH_3.CH_2.I, \quad CH_3I \ \text{ and } \ CH_3I, \quad CH_2I_2, \quad CHI_3.$$

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).

Using the ordinary expression for the absolute rate of a bimolecular reaction, we find for the interchange reaction $CH_3I + I^-$ in alcohol an activation energy of 16.5 Kcal. as an upper limit. This is of interest in connection with the recent theoretical discussion[1] of such reactions by Ogg and Polanyi.

F. JULIUSBURGER

B. TOPLEY

J. WEISS

The Sir William Ramsay Laboratories
    of Inorganic and Physical Chemistry,
  University College,
    Gower Street,
      London, W.C. 1,
      May 17, 1935.

[1] See Ogg and Polanyi, Trans. Faraday Soc. 31, 604 (1935).

The Difference in the Heats of Formation of the Two Isomers of Butane. An Estimate of the Heat of Formation of Tetramethylmethane (Neopentane)[1]

Data recently obtained in this laboratory on the heat of combustion of isobutane can be combined with similar data on normal butane[2] to yield a reliable value for the difference in the energies of formation of the two isomers.

The calorimetric experiments on both normal butane and isobutane were made with the same apparatus and procedure, and both hydrocarbons used in the measurements were of established purity. For these reasons, the reliability of the relatively small difference in the two values of the heats of combustion will be determined by the "precision" uncertainty of the calorimetric combustion experiments, rather than by the "accuracy" uncertainty. In the two series of calorimetric combustion experiments, the "precision" uncertainties were ± 0.12 and ± 0.09 kilocalorie per mole for normal butane and isobutane, respectively. Taking the resulting uncertainty in the difference of the two heats of combustion as the square root of the sum of the squares of the foregoing quantities, the data yield, at 25°C and 1 atmosphere, for the reaction,

$$n-C_4H_{10}(gas) = iso-C_4H_{10}(gas),$$
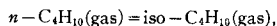
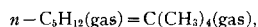$$\Delta H_{298.1} = -1.63 \pm 0.15 \text{ kilocalories per mole.}$$

Since for these isomers, at room temperature and a pressure of 1 atmosphere, the difference in the values of PV, and of $E(p=1) - E(p=0)$, is not significant, one may write for the same reaction

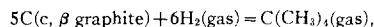$$\Delta H^0_{298.1} = E^0_{298.1} = -1.63 \pm 0.15 \text{ kilocalories per mole.}$$

ΔH and ΔE are, respectively, the increments in the heat content and in the internal or intrinsic energy.

The value of the heat of combustion of isobutane (trimethylmethane) can be used in conjunction with the values already reported[2,3] for methane, ethane (monomethylmethane), and propane (dimethylmethane) to deduce a fairly reliable value for the heat of combustion of tetramethylemethane (neopentane). By plotting $(Qc-A)/n$ (where Qc is the heat of combustion, A is a constant whose value was taken as 52.00, and n is the number of carbon atoms in the molecule) against n, one obtains a smooth curve which can be extrapolated to $n=5$ with some confidence. Assigning a reasonable limit of error, one obtains for the heat of combustion of gaseous tetramethylmethane, $C(CH_3)_4$, in oxygen to form gaseous carbon dioxide and liquid water, at 25°C and a constant pressure of 1 atmosphere, the value 840.4 ± 1.0 kilocalories per mole. This value is about 6 kilocalories per mole less than the one experimental value extant in the literature, that of Thomsen[4] reported in 1886. Thomsen's tetramethylmethane was impure, his samples having the empirical formulas of $C_5H_{11.64}$ and $C_5H_{11.78}$, instead of C_5H_{12}. This thermochemical constant will be redetermined experimentally as soon as material of the necessary purity is obtained.
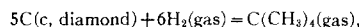
Combination of the foregoing value for tetramethylmethane with the values recently reported for normal pentane,[2,3] yields the following:

$$n-C_5H_{12}(gas) = C(CH_3)_4(gas),$$

$$\Delta H^0_{298.1} = \Delta E^0_{298.1} = -4.9 \pm 1.0 \text{ kilocalories per mole;}$$

$$5C(c, \beta \text{ graphite}) + 6H_2(gas) = C(CH_3)_4(gas),$$

$$\Delta H^0_{298.1} = -40.7 \pm 1.2 \text{ kilocalories per mole;}$$

$$5C(c, \text{ diamond}) + 6H_2(gas) = C(CH_3)_4(gas),$$

$$\Delta H^0_{298.1} = -41.8 \pm 1.2 \text{ kilocalories per mole.}$$

FREDERICK D. ROSSINI

National Bureau of Standards,
  Washington, D. C.,
    June 10, 1935.

[1] Publication approved by the Director of the National Bureau of Standards, U. S. Department of Commerce.
[2] Rossini, Bur. Standards J. Research 12, 735 (1934).
[3] Rossini, J. Research Nat. Bur. Standards 13, 21 (1934).
[4] Thomsen, Thermochemische Untersuchungen, Vol. IV (Barth, Leipzig, 1886).