$CH_3\cdot H$ and $H\cdot H$ represent interactions between non-bonded groups along the edges of the ethylenic rectangle which are perpendicular to the double bond, and $H:H$ and $CH_3:H$ those interactions between non-bonded groups along the edges of the rectangle which are parallel to the double bond. For purposes of calculation it is convenient to rearrange equation (3) into an equivalent form which is

$$\begin{aligned}\chi = {} & 3[1/4C{=}C + H + 1/2H\cdot H + 1/2H:H] \\ & + [1/4C{=}C + CH_3 + 1/2CH_3\cdot CH_3 + 1/2CH_3:CH_3] \\ & + [CH_3\cdot H - 1/2CH_3\cdot CH_3 - 1/2H\cdot H] \\ & + [CH_3:H - 1/2CH_3:CH_3 - 1/2H:H] \qquad (4)\end{aligned}$$

The equation again contains two classes of groups. However, we now have four adjustable constants owing to the fact that two edges of the ethylenic rectangle are different. The values for these groups which were calculated by the methods of least squares from the experimental data in Table IB are listed in Table IVA.

Similar equations were used for the heats of formation given in Table IIB. The bond and interaction energies are listed in Table IVB. The data in this table were used in equations of the type 4 to calculate molar susceptibilities and heats of formation. The results are given in Tables IB and IIB, columns four. The agreement between the experimental and calculated values is quite good. The equations will reproduce the small differences between the *cis*-, *trans*- and 1,1-isomers.

TABLE IV

METHYL DERIVATIVES OF ETHYLENE

A. Group and interaction susceptibilities

	$-\chi \times 10^6$
$1/4C{=}C + H + 1/2H\cdot H + 1/2H:H$	5.10
$1/4C{=}C + CH_3 + 1/2CH_3\cdot CH_3 + 1/2CH_3:CH_3$	16.47
$H\cdot CH_3 - 1/2H\cdot H - 1/2CH_3\cdot CH_3$	−0.42
$H:CH_3 - 1/2H:H - 1/2CH_3:CH_3$	0.47

B. Bond and interaction energies

	ΔH, kcal.
$1/4C{=}C + H + 1/2H\cdot H + 1/2H:H$	−132.85
$1/4C{=}C + CH_3 + 1/2CH_3\cdot CH_3 + 1/2CH_3:CH_3$	−120.09
$H\cdot CH_3 - 1/2H\cdot H - 1/2CH_3\cdot CH_3$	0.30
$H:CH_3 - 1/2H:H - 1/2CH_3:CH_3$	−0.75

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[CONTRIBUTION FROM THE NATIONAL BUREAU OF STANDARDS AND THE CATHOLIC UNIVERSITY OF AMERICA]

Pyrolysis of Mixtures of Ethane and Ethane-d_6[1]

BY LEO A. WALL AND WALTER J. MOORE

The pyrolysis of 50–50 mixtures of ethane and ethane-d_6 has been investigated between 510 and 610° by mass spectrometric analyses of the products. The extensive isotopic mixing that is observed in the products indicates that free radicals and hydrogen atoms occur in the decomposing mixture. The presence of nitric oxide inhibits the reaction rate and decreases the extent of isotopic mixing. It seems probable that part of the NO-inhibited reaction proceeds *via* an intramolecular mechanism, and part *via* a free-radical mechanism. In the mixtures of C_2H_6 and C_2D_6, the over-all decomposition rate of the light ethane is about 50% faster than that of the heavy ethane. This factor is in reasonable agreement with a value based on the dominant influence of the difference in zero-point energies of C–H and C–D bond vibrations. The production of CD_3 radicals from C_2D_6 is about five times faster than the production of CH_3 radicals from C_2H_6. This effect is due primarily to the greater density of rotational states of CD_3 as compared to CH_3, which lowers the activation entropy for heavy-radical formation.

The thermal decomposition of ethane has been studied by many workers since the first investigation by Pease,[2] yet it cannot be said that the reaction is satisfactorily understood. One outstanding problem concerns the proportion of the reaction that proceeds *via* a free-radical mechanism and the proportion that proceeds *via* a molecular rearrangement. In an attempt to elucidate this problem, the pyrolysis of mixtures of C_2H_6 and C_2D_6 has been followed by mass-spectrometric analyses of the products.

Experimental

The ethane used had a purity of better than 99%. The ethane-d_6 was prepared by deuteration[3] of C_2D_2 with D_2 over a nickel–asbestos catalyst. The C_2D_2 was a product of the action of 99.8% D_2O on calcium carbide previously baked for 48 hr. at 1200° under high vacuum. Mass spectrometric analysis showed the ethane component to be greater than 99% C_2D_6, but there was an admixture of 3% deuterated propane and butane.

The C_2H_6 and C_2D_6 were mixed in approximately equal amounts in 25-ml. reaction vessels. The initial pressure was about 600 mm. at the reaction temperature. In some experiments nitric oxide was added to the reaction mixture. Vessels of Pyrex, quartz, and KCl-coated Pyrex were used; they were cleaned between successive runs by heating in air for 12 hr. at 500°. After being sealed while the reactants were chilled in liquid nitrogen, the vessels were introduced into a muffle furnace regulated to ±5°. Vessels were withdrawn from the furnace at intervals, and the products admitted directly to the mass spectrometer (Consolidated) by breaking an attached capillary. The analyses were performed by the Mass Spectrometer Section of the National Bureau of Standards.

Results

Pyrolysis of C_2H_6 Alone.—A number of runs were made with C_2H_6 in various reaction vessels, and in the presence and absence of nitric oxide. Even at large conversions, the products were almost entirely H_2, C_2H_4 and CH_4. A few tenths of one per cent. of C_3H_6 and C_3H_8 were detected; C_4 and C_5 hydrocarbons were virtually absent. Typical analytical results are shown in Table I. In the packing experiments Pyrex-glass wool was used to increase the surface to volume ratio by a factor of about 50. It may be noted that at 615°

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[1] Presented in part at the 116th Meeting of the American Chemical Society, Atlantic City, N. J., September, 1949.

[2] R. N. Pease, THIS JOURNAL, **50**, 1779 (1928). A review of subsequent work is given by E. W. R. Steacie, "Atomic and Free Radical Reactions," Reinhold Publishing Corp., New York, N. Y., 1946, p. 90–103.

[3] The deuterium and deuterium oxide used in this investigation were supplied by the Stuart Oxygen Company, and obtained on allocation from the Isotopes Division, U. S. Atomic Energy Commission.

TABLE I

PYROLYSIS OF ETHANE IN PYREX VESSELS AT 615°

Component	Time, min.	Mole per cent. of products: Without packing 5	10	20	With packing 5	10	20	With 5% NO 5	10	20	40
H_2		4.0	15.0	13.8	11.3	17.1	18.3	1.1	19.2	19.6	15.5
C_2H_4		4.4	13.2	11.3	6.3	9.1	13.6	3.1	14.8	11.6	6.9
CH_4		0.2	3.8	6.5	3.8	6.5	19.5	0.4	9.3	32.6	53.4
C_2H_6		90.9	67.1	67.3	76.6	65.1	46.8	95.0	55.7	35.3	23.1

the equilibrium $C_2H_6 = C_2H_4 + H_2$ lies at 19% C_2H_4 (from thermodynamic data), and the half-life of the forward reaction, from the data of Steacie and Shane,[4] is 15 min.

The data in Table I display an acceleration of the reaction by packing, but the relative increase in the rate is much less than that in the available surface. Packing appears to enhance the rate of formation of methane. Experiments in quartz or KCl-coated Pyrex vessels yielded essentially the same results as those in unpacked Pyrex. In the more extensive runs a brown carbonaceous deposit appeared on the walls of the reaction vessels.

The inhibitory effect of added nitric oxide appears to be limited to the first five minutes of the reaction, and after five minutes nitric oxide itself no longer appears in the analyses. Nevertheless, the rate of formation of methane is considerably enhanced in the later stages of the runs with added nitric oxide.

Pyrolysis of $C_2H_6 + C_2D_6$: The Hydrogen Analyses.—Mixtures of 54% C_2H_6 and 46% C_2D_6 were decomposed at 510, 560 and 610° in clean quartz and Pyrex vessels. No significant differences were noted between the results in quartz and Pyrex. Hydrogen analyses from the initial stages of the reactions are summarized in Table II.

TABLE II

ISOTOPIC COMPOSITION OF HYDROGEN FROM PYROLYSIS OF $C_2H_6 + C_2D_6$, MOLE PER CENT.

	510°, 2.2 hr.	520°, 2.5 hr. 2.5% NO	560°, 10 min.	610°, 4 min.	610°, 4 min. 2.5% NO	610°, 4 min. packed
H_2	40.4	42.7	41.3	40.4	49.8	45.0
HD	45.1	42.7	45.1	44.4	35.8	43.6
D_2	14.5	14.6	13.6	15.2	14.4	11.4
H/D	1.70	1.78	1.77	1.67	2.09	2.01
Q	3.47	2.92	3.62	3.21	1.78	2.69

Since the H/D ratio of the reactants is 1.17, and that of the products is about 1.72, there is evidently a marked isotope effect on the rate of hydrogen production. In the mixture, the rate of decomposition of the C_2H_6 is 47% faster than that of the C_2D_6. In the presence of added nitric oxide, the C_2H_6 rate appears to be 78% higher than the C_2D_6 rate.

Included in Table II are the values of $Q = (HD)^2/(H_2)(D_2)$. For complete equilibrium among the hydrogen molecules, Q is about 3.80 at these temperatures.[5] The observed values of Q indicate that isotopic mixing is nearly complete even in the initial stages of the pyrolytic reaction. In the runs with added nitric oxide, there is still considerable mixing, but it is much less complete. Packing the reaction vessel also seems to decrease the extent of mixing of the isotopic hydrogens.

Mixing Reactions of H_2 and D_2.—Separate runs were made to determine the mixing of $H_2 + D_2$, $D_2 + CH_4$, $H_2 + CD_4$, and $CH_4 + CD_4$. The detailed analyses are reported elsewhere.[6] Even after one hour at 600° the Q value for $H_2 + D_2$ is only 0.70, and the formation of HD from $CH_4 + D_2$ or $CD_4 + H_2$ amounted to only a few per cent. Mixing of CH_4 and CD_4 was negligible in one hour at 600°. These results demonstrate that when extensive isotopic mixing of the products occurs in the decomposition of the mixed ethanes, it is the result of reactions connected with the decomposition process and not of secondary mixing of the final products.

Pyrolysis of $C_2H_6 + C_2D_6$: The Methane Analyses.—The mass spectrometric analysis of the deuterated methanes is capable of high precision, because patterns for all five methanes have been obtained.[7] The isotopic compositions of the methanes from the $C_2H_6 + C_2D_6$ mixtures are shown in Figs. 1 and 2. It should be noted that the H/D ratio in the methanes is always well below unity, whereas in the hydrogens the ratio is always greater than unity. For example, after 4 min. reaction at 610°, H/D = 0.41 for the methanes and H/D = 1.67 for the hydrogens. In the presence of 2.5% nitric oxide, these figures are 0.33 and 2.09. The addition of nitric oxide lowers the methane ratio and raises the hydrogen ratio. The addition of nitric oxide does not greatly inhibit the mixing of the methanes, and the products from the inhibited reaction are those that would be expected if the time scale were expanded without much change in the mechanism.

Pyrolysis of $C_2H_6 + C_2D_6$, Ethane Mixing.—It is not as yet possible to analyze a complex mixture of the deuterated ethylenes and ethanes, but the relative concentrations of certain compounds in such a mixture can be determined with considerable accuracy. For example, the ratio of the mass peaks 36/35 gives a measure of the C_2D_6/C_2D_5H ratio. This figure provides a useful indication of the extent of the back reaction, $C_2D_4 + HD = C_2D_5H$. Based on $C_2D_6 = 1$, the relative amounts at various times of C_2D_5H, $C_2D_4H_2$ and $C_2D_3H_3$, as determined from the mass peaks, are shown in Figs. 3 and 4. The effect of nitric

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(4) E. W. R. Steacie and G. Shane, *Can. J. Research*, **B18**, 351 (1940).

(5) H. W. Woolley, R. B. Scott and F. G. Brickwedde, *J. Research Natl. Bur. Standards*, **41**, 379 (1948).

(6) L. A. Wall and W. J. Moore, "The Use of Deuterium in Elucidating the Mechanisms of Decomposition of Organic Compounds," American Chemical Society Symposium on Anomalies in Reaction Kinetics, Minneapolis, Minn., June, 1950.

(7) V. H. Dibeler and F. L. Mohler, "Mass Spectra of the Deuteromethanes," 118th Meeting of the American Chemical Society, Chicago, Ill., September, 1950.

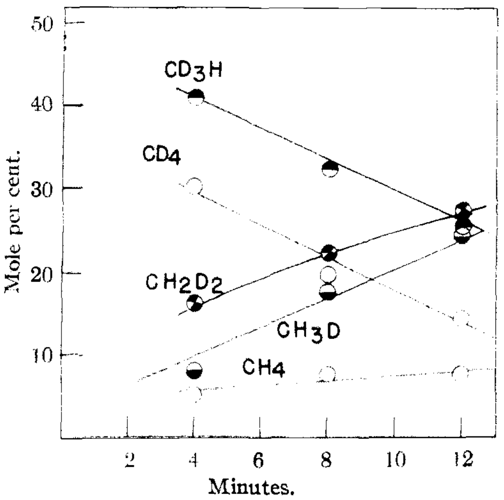

Fig. 1.—Isotopic composition of methanes from pyrolysis of $C_2H_6 + C_2D_6$ at 610°.

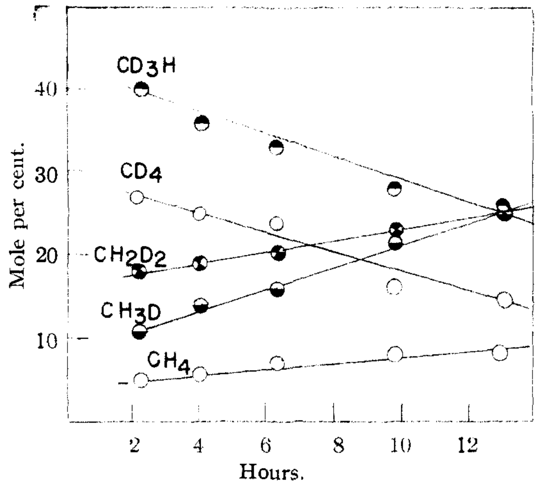

Fig. 2.—Isotopic composition of methanes from pyrolysis of $C_2H_6 + C_2D_6$ at 510°.

oxide in inhibiting the formation of mixed ethanes in the early stages of the 610° runs may be especially noted. It should also be noted that the mixing of the ethanes after 4 min. at 610° is much less extensive than the mixing observed in the hydrogen and methane fractions of the reaction products.

Discussion

The extensive isotopic mixing of the products from the ethane pyrolysis is evidence for the occurrence of radicals and hydrogen atoms in the reaction mixture. The intramolecular decomposition of $C_2H_6 + C_2D_6$ mixtures would proceed as

$$C_2H_6 = C_2H_4 + H_2,\quad C_2D_6 = C_2D_4 + D_2$$

It provides no direct mechanism for the mixing of the hydrogens. The chain mechanism proposed by Rice and Herzfeld[8] does provide a convenient interpretation of the mixing

$$C_2H_6 = 2CH_3 \tag{1a}$$
$$C_2D_6 = 2CD_3 \tag{1b}$$
$$CH_3 + C_2H_6 = CH_4 + C_2H_5 \tag{2a}$$
$$CD_3 + C_2D_6 = CD_4 + C_2D_5 \tag{2b}$$
$$CD_3 + C_2H_6 = CD_3H + C_2H_5 \tag{3a}$$
$$CH_3 + C_2D_6 = CH_3D + C_2D_5 \tag{3b}$$
$$C_2H_5 = C_2H_4 + H \tag{4a}$$
$$C_2D_5 = C_2D_4 + D \tag{4b}$$
$$H + C_2H_6 = C_2H_5 + H_2 \tag{5a}$$
$$D + C_2D_6 = C_2D_5 + D_2 \tag{5b}$$
$$H + C_2D_6 = C_2D_5 + HD \tag{6a}$$
$$D + C_2H_6 = C_2H_5 + HD \tag{6b}$$

In addition to the mixing caused by the chain processes, the hydrogen atoms will promote rapid mixing of the hydrogen molecules through reactions of low activation energy such as $H + D_2 = HD + D$, $D + H_2 = HD + H$. Even a low concentration of H atoms would suffice to produce the observed mixing (Appendix 1). Thus, even if only a small part of the reaction proceeded *via* a chain mechanism involving H atoms, mixing of the product hydrogens would still be expected. The results of nitric oxide inhibition,[9] however,

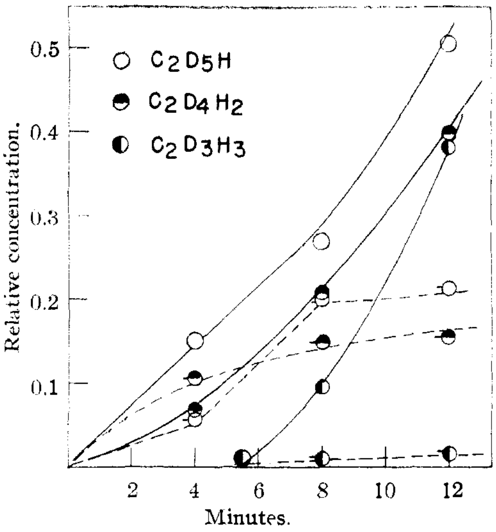

Fig. 3.—Isotopic composition of ethanes from pyrolysis of $C_2H_6 + C_2D_6$ at 610°; dotted curves, 2.5% NO added.

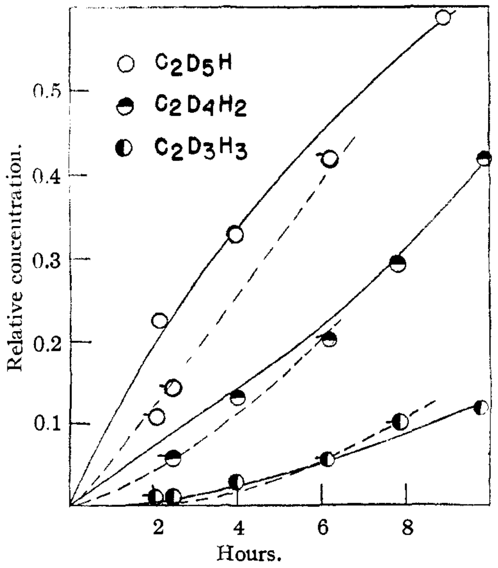

Fig. 4.—Isotopic composition of ethanes from pyrolysis of $C_2H_6 + C_2D_6$ at 510°; dotted curves, 2.5% NO added

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[8] F. O. Rice and K. F. Herzfeld, THIS JOURNAL, **56**, 284 (1934).

[9] J. E. Hobbs and C. N. Hinshelwood, *Proc. Roy. Soc. (London)*, **A167**, 447 (1938); E. W. R. Steacie and G. Shane, *Can. J. Research*, **18**, 351 (1940).

demonstrate that a major fraction of the pyrolysis proceeds *via* a free-radical pathway.

In order for the conclusion that extensive mixing indicates the occurrence of atoms and/or radicals to be valid, it must be shown that the observed mixing cannot occur through a sequence of molecular decompositions and recombinations, such as

$$C_2H_6 = C_2H_4 + H_2 \qquad (7a)$$

$$C_2D_6 = C_2D_4 + D_2 \qquad (7b)$$

$$C_2D_4 + H_2 = C_2D_4H_2 \qquad (8a)$$

$$C_2H_4 + D_2 = C_2H_4D_2 \qquad (8b)$$

$$C_2D_4H_2 = C_2D_3H + HD \qquad (9a)$$

$$C_2H_4D_2 = C_2H_3D + HD \qquad (9b)$$

In the early stages of reaction the observed $C_2D_4H_2$ analyses are too low to account for the observed mixing. In addition it can be shown from the known rate constants that mixing by way of back reactions is too slow to account for the observed products (Appendix 2).

The Effect of Nitric Oxide.—The rate of pyrolysis of a hydrocarbon in the presence of enough nitric oxide to effect maximal inhibition has usually been ascribed to an intramolecular decomposition of the hydrocarbon. According to this view, nitric oxide can prevent virtually all free-radical chains, and does not itself react with the hydrocarbon.[10] In the present experiments, the addition of nitric oxide definitely inhibits the isotopic mixing of the products, yet this mixing remains extensive even in the initial stages of the reaction. Therefore, it does not appear likely that nitric oxide completely inhibits the formation of free radicals and hydrogen atoms, at least in a mixture of C_2H_6 and C_2D_6. It is quite possible that added nitric oxide initiates chains: NO + $C_2H_6 = C_2H_5 +$ NOH. In this event, chain lengths estimated from the ratio of uninhibited to maximally inhibited reaction rate would have no quantitative significance.

The question of possible surface reactions remains open. The present studies were made in clean quartz or Pyrex vessels, without "conditioning," or the deliberate deposition of a carbonaceous coating. Under these conditions it is possible that some free-radical chains may be initiated at the surface,[11] and some of the mixing in the presence of nitric oxide may be due to surface reactions. In packed vessels, the observed isotopic mixing of hydrogens, methanes and ethanes, does not differ significantly from that in unpacked vessels. This result provides indirect evidence that most of the observed mixing occurs through homogeneous reactions. In general, effects due to surface reactions tend to be of minor importance at temperatures and pressures as high as those employed in this investigation.

Isotope Effects

The high H/D ratio in the hydrogen product from the pyrolysis of mixed ethanes can be explained by the difference between the activation energies of reactions that break a C–H bond and those that break a C–D bond (*e. g.*, reactions (4a) and (4b)). It is easier to break a C–H bond than to break a C–D bond, owing to the lower zero-point energy of the vibration of the latter. If the C–H stretching vibration frequency is taken to be 2963 cm.$^{-1}$, and the C–D frequency, 2225 cm.$^{-1}$, the difference in zero-point energies is 1050 cal.[12] An activation-energy difference of this amount would correspond to a rate ratio of 1.82 at 610°, in reasonable agreement with the observed results.[13]

The striking reversal of the isotope effect in the methanes indicates that it is considerably easier for C_2D_6 to yield CD_3 radicals than it is for C_2H_6 to yield CH_3 radicals. In a mixture of C_2H_6 and C_2D_6 the chain-initiating radicals are predominantly CD_3. The initial ratio of (CD_3H + CD_4) to (CH_3D + CH_4) is 5.5 at 610° and 4.2 at 510°. This large effect appears to be due primarily not to a difference in activation energies but to a difference in activation entropies.

Gorin[14] has derived an expression for the rate of combination of methyl radicals, and Gorin, Kauzmann, Walter and Eyring[15] have combined this expression with the equilibrium constant, $k_f/k_b = K = f^2_{CH_3}/f_{C_2H_6}$ (f being the partition function) to calculate $k_f = k_bK$ for $C_2H_6 = 2CH_3$. For the ratio of the recombination rate of CH_3 to that of CD_3, the expression of Gorin yields $(18/15)^{1/2} = 1.09$ (Appendix 3). If vibrational contributions to the partition functions are ignored, the ratio of the K for C_2H_6 dissociation to that for C_2D_6 dissociation is 0.254. The calculated ratio of the k_f's for CD_3 and CH_3 formation from the respective ethanes is, therefore, 3.6 (Appendix 3). This figure agrees quite well with the experimental estimate of 4.8.

The physical reason for the large isotope effect is the following: Since the methyl radicals almost certainly have a planar structure,[16] with the axes of rotation passing through the central carbon atom, the entire effect of the D/H mass ratio is carried over into the moments of inertia, and hence into the rotational partition functions. The density of rotational states is greater for CD_3 than for CH_3, and since the recombination rates are not very different, the resultant entropy factor greatly favors the formation of heavy radicals. This result also suggests that the decomposition kinetics of a mixture of C_2H_6 and C_2D_6 may not furnish an exact model for the decomposition of C_2H_6 alone, since the heavy ethane is a more ready source of free radicals.

Appendix I

Mixing of Hydrogens by Hydrogen Atoms.—Consider the reaction H + D_2 = HD + D, with $d(HD)/dt = k_1(H)(D_2)$. An upper limit for the extent of HD formation can be obtained by setting (D_2) equal to its value after 4 min. reaction at 610°. Then, using the observed value of k_1,[17] one ob-

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[10] The most recent evidence for this theory is contained in a paper by F. J. Stubbs and C. N. Hinshelwood, *Proc. Roy. Soc.* (*London*), **A200**, 458 (1950).

[11] F. O. Rice and K. F. Herzfeld, "The Mechanism of Some Chain Reactions," American Chemical Society Symposium on Anomalies in Reaction Kinetics, Minneapolis, Minn., June, 1950.

[12] G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., New York, N. Y., 1945, p. 345.

[13] The enhanced H/D ratio in the presence of nitric oxide might be interpreted as an indication that there is a greater isotope effect in a residual intramolecular reaction.

[14] E. Gorin, *Acta Physicochim. U. R. S. S.*, **9**, 691 (1938).

[15] E. Gorin, W. Kauzmann, J. Walter and H. Eyring, *J. Chem. Phys.*, **7**, 633 (1939).

[16] C. A. Coulson, Discussions of the Faraday Society, No. 2, 9 (1947); A. D. Walsh, *ibid.*, 18.

[17] A. Farkas and L. Farkas, *Proc. Roy. Soc.* (*London*), **A152**, 124 (1935).

tains (HD) = 9.2×10^7 (H) at end of 4 min. Even with the low value of (H) obtained by Patat and Sachsse,[18] 10^{-11} mole/liter, the formation of HD by this mechanism is rapid enough to account for the observed concentration at the end of 4 min., (HD) = 2×10^{-4}.

Appendix 2

Mixing of Hydrogens by Molecular Back Reactions.—Consider reactions (7), (8) and (9), and let the over-all rate constant for any ethane decomposition be k_1, and for any combination of ethylene and hydrogen be k_2. In the early stages of reaction $d(C_2H_4D_2)/dt = k_2(D_2)(C_2H_4)$. A maximum rate of formation of the mixed ethane over the time interval can be estimated by setting $(D_2) = (C_2H_4)$ equal to its final value (b), *e.g.*, at the end of 4 min. at 610°. Then $(C_2H_4D_2) = k_2b^2t$. Since $d(HD)/dt = k_1(C_2H_4D_2)$, $(HD) = {}^1/_2k_1k_2b^2t^2$. This value of (HD) would be the maximum obtainable through a sequence of forward and reverse reactions. From the work of Steacie and Shane[4] and the calculated equilibrium constant, $k_1 = 7.4 \times 10^{-4}$ sec.$^{-1}$, and $k_2 = 1.4$ lit.$^{-1}$ sec.$^{-1}$ mole, at 610°. At the end of 4 min. there is 4% H_2 or 4.3×10^{-4} mole/liter, and hence (HD) = 1.1×10^{-5}, or 2.6% of the isotopic hydrogens. Experimentally one finds 44% HD under these conditions. It may be noted that back-mixing becomes even less likely at lower temperatures (for comparable extents of reaction). For example, at 537° and a time of 30 min. the calculated % HD would be only 0.2%, whereas the observed is 45%.

Appendix 3

The Relative Rates of Dissociation of C_2H_6 and C_2D_6 into **Methyl Radicals.**—The equation of Gorin for the rate of combination of two methyl radicals is

$$k_b = 8\kappa\Gamma({}^2/_3)(kT)^{1/6}(3\alpha^2\mathcal{J}/2)^{1/3}(\pi/m)^{1/2}\sigma^{-1}$$

Here α is the polarizability, κ the transmission coefficient, $\mathcal{J}$ the ionization potential, σ the symmetry number, and m the mass of the radicals. In comparing CH_3 and CD_3 radicals only the masses are significantly different, so that the rate ratio is $(18/15)^{1/2} = 1.09$.

The equilibrium constant for the dissociation is $K = f^2_{CH_3}/f_{C_2H_6}$. If vibrational terms are ignored,

$$K = \frac{\left[\dfrac{8\pi^2(8\pi^3I_z^2I_x)^{1/2}}{\sigma h^3}\cdot\dfrac{(2\pi mkT)^{3/2}}{h^3}\right]^2_{CH_3}}{\left[\dfrac{8\pi^2(8\pi^3I_z^2I_x^{1/2})}{\sigma h^3}\cdot\dfrac{(2\pi mkT)^{3/2}}{h^3}\right]_{C_2H_6}}$$

Then

$$K_{C_2H_6}/K_{C_2D_6} = \frac{m^3_{CH_3}m^{3/2}_{C_2D_6}}{m^3_{CD_3}m^{3/2}_{C_2H_6}}\cdot\frac{I^3_{CH_3}}{I^3_{CD_3}}\cdot\frac{(I_z^2I_x)^{1/2}_{C_2D_6}}{(I_z^2I_x)^{1/2}_{C_2H_6}}$$

$$= (0.760)(0.125)(1.414)I_{zC_2D_6}/I_{zC_2H_6}$$

The ratio of I_z for the ethanes is 1.35. Although vibrations have been neglected, it would be a good approximation at these temperatures to add a factor of $2^{1/2}$ to take into account the isotope effect on the internal rotations of the methyl groups. One, therefore, obtains $K_{C_2H_6}/K_{C_2D_6} = 0.254$. The ratio of the forward rates is then 3.6.

Another factor that may influence the isotopic composition of the methanes from the pyrolysis of $C_2H_6 + C_2D_6$ is the relative rate of the hydrogen-abstraction reaction with light and heavy methyl radicals. Trotman-Dickenson and Steacie[19] have studied the reaction of CD_3 radicals, from the photolysis of acetone-d_6, with neopentane. If the reaction $2CH_3 = C_2H_6$ is taken to be 9% faster than $2CD_3 = C_2D_6$ (from the equation of Gorin), the abstraction of a hydrogen atom by CD_3 would be about 7% slower than that by CH_3. This effect would tend to raise the stationary-state concentration of CD_3 compared to CH_3, but only by a small factor.

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[18] F. Patat and H. Sachsse, *Z. Elektrochem.*, **41**, 493 (1935).

[19] A. F. Trotman-Dickenson and E. W. R. Steacie, "The Reactions of Methyl Radicals," American Chemical Society Symposium on Anomalies in Reaction Kinetics, Minneapolis, Minn., June, 1950.

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[Contribution from the Hayden Memorial Laboratories of Northeastern University]

The Solubility of Tetraethylammonium Chloride in Benzene–Ethylene Dichloride Mixtures

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The solubility of tetraethylammonium chloride was determined for benzene–ethylene dichloride mixtures in the range of dielectric constant from 10.36 to 4.25. In this range the log *S*–log *D* plot is a straight line with a slope of about 7.

Introduction

Vernon and Sheard[2] reported the solubility of tetraethylammonium iodide in benzene–ethylene dichloride mixtures and found that a plot of logarithm of solubility against logarithm of dielectric constant gave a straight line with a slope of about five. In order to test this relationship for another solute, studies were made with tetraethylammonium chloride.

Experimental

Materials.—C.P. thiophene-free benzene was stored over anhydrous calcium chloride for several days and was then distilled over phosphorus pentoxide in a fractionating column, discarding the first and last fifths. The refractive index at 25.2° was 1.4978 compared with the "International Critical Tables" value of 1.49779.

Ethylene dichloride was stored over anhydrous calcium chloride and distilled from fresh anhydrous calcium chloride, discarding the first and last fifths. The index of refraction at 25.2° was 1.4422 compared to the "International Critical Tables" value of 1.44225.

Tetraethylammonium chloride was prepared by two methods. In the first method triethylamine was allowed to react with one hundred per cent. excess of ethyl chloride in 95% alcohol for three weeks. During this time the reaction flask was connected to a condenser through which ice water was circulated in order to keep the ethyl chloride loss to a minimum. After the completion of the reaction the solvent was evaporated and the solid was dried in a vacuum oven at 120° for 48 hours. The product analyzed 21.37 per cent. of chlorine by Volhard titration as compared to the theoretical 21.41 per cent.

A second method was developed which was shorter and more economical. Fifty per cent. excess of solid mercurous chloride was added to a 40 per cent. water solution of tetraethylammonium iodide and the mixture was kept at 60° for one week while stirring. The solid was removed by filtration and the filtrate was evaporated to one-half its volume with an additional 25 per cent. of mercurous chloride in order to insure completion of the reaction. The presence of unreacted iodide would be shown by a color change from the white of Hg_2Cl_2 to the greenish-brown of Hg_2I_2. After filtration, the solution was evaporated to dryness and the product dissolved in a small amount of 95 per cent. ethyl alcohol to precipitate any unreacted tetraethylammonium iodide. The solution was again filtered, evaporated to dryness, and the solid was dissolved in warm ethylene dichloride in the proportion of 20 cc. of solvent per gram of solid. The final purified product was crystallized in an ice-bath

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