Errata: Magnetic Study of Some Organometallic Compounds of Arsenic

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elementary reaction

$$H + RH = H_2 + R. \qquad (1)$$

However, the determination of rate constants, steric factors, and activation energies for such reactions involves a number of difficulties which have an important bearing on the accuracy of the values obtained.

Since the rate of (1) would be given by the expression

$$\mathfrak{R} = k[H][RH], \qquad (2)$$

the determination of k requires a knowledge of $\mathfrak{R}$, [H], and [RH]. Most of the published data have been obtained by the Wood-Bonhoeffer method.[1] $\mathfrak{R}$ is equated to the rate of consumption of paraffin; [H] is measured in a fixed position in the reactor and is assumed to have a constant value throughout the reaction zone; either initial or average values are used for [RH]. In a few cases average values of [H] were used,[2] based on measurements at the top and bottom of the reactor. In no case was allowance made for recombination of H-atoms.

It is clear that if a recombination reaction of the type

$$R + H(+M) = RH(+M) \qquad (3)$$
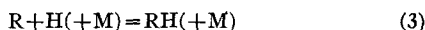
occurs, the value of $\mathfrak{R}$ used will be too small. Also [H] will decrease approximately exponentially with time, and even its average value will yield a low value for k; the assumption about [RH] will have the same effect. The magnitude of the error in k arising from the above assumptions, as well as certain others which will not be discussed here, will depend on the particular paraffin and the experimental conditions used, but in general the calculated values will be low.

It might be anticipated that the error in k would have little effect on the activation energy E, calculated from the temperature coefficient through the relation

$$k = pZe^{-E/RT}. \qquad (4)$$

However, only a very few studies have been made of the effect of temperature on k. The practice has been to assume that $p = 0.1$ and to calculate E from data for a single temperature. This is clearly open to criticism, and in recent papers[2,3] evidence has been put foreward suggesting that p might be considerably less than 0.1.

The difficulties outlined above have been largely eliminated by using the method of Dingle and LeRoy[4] for the production and detection of atomic hydrogen. Our results for ethane will be reported here in brief.

By increasing the area of the detector it was possible to remove all of the H-atoms from the stream at that point and to calculate the absolute value of [H] at any time (position in the reactor). Methane was the only product, and measurement of the amount produced up to any position of the detector permitted the calculation of [C₂H₆] as a function of time. Allowance was made for the recombination of H-atoms. From the quantity of ethane and atomic hydrogen consumed it was possible to measure the extent of reaction (3) and thus to obtain the true value of $\mathfrak{R}$.

Values of k were obtained in this way for four temperatures in the range 80° to 163°C. The collision diameters were taken to be

TABLE I. Comparison of rate constants for the reaction $H + C_2H_6 = H_2 + C_2H_5$ at room temperature.[a]

Authors	Reaction	Collision yield $\times 10^8$	k cm³ molec⁻¹ sec⁻¹ $\times 10^{17}$
Chadwell and Titani[b]	$H + C_2H_6$	1.8	1.2
Steacie[c]	$H + C_2H_6$	3.3	2.2
Trost and Steacie[d]	$H + C_2H_6$	2.0	1.3₅
Trost and Steacie[d]	$D + C_2H_6$	3.0	2.0₂
Taylor et al.[e]	$D + C_2H_6$	6.2	4.1₅
Berlie and LeRoy	$H + C_2H_6$	9.4	6.3₉

[a] The first five values of k were calculated from the data of Table IV, reference 2 by the relation $k = Z \times$collision yield.
[b] H. M. Chadwell and T. Titani, J. Am. Chem. Soc. 55, 1363 (1933).
[c] E. W. R. Steacie, J. Chem. Phys. 6, 37 (1938).
[d] See reference 2.
[e] Trenner, Morikawa, and Taylor, J. Chem. Phys. 5, 203 (1937).

the same as those used by Trost and Steacie.[2] From the plot of $\log(k/Z)$ vs $1/T$ the activation energy of reaction (1) was found to be 6.2 ± 0.1 kcal per mole, the steric factor to be 3.3×10^{-3}.

For comparison, a value of k for 24°C was calculated from Eq. (4) using our values of p and E. From Table I it is seen that this is larger than the values obtained by other workers, as predicted. Full details of this work will appear in a later publication.

The authors are indebted to the Associate Committee on Scientific Research of the University of Toronto for financial assistance.

[1] E. W. R. Steacie, Atomic and Free Radical Reactions (Reinhold Publishing Corporation, New York, 1946).
[2] W. R. Trost and E. W. R. Steacie, J. Chem. Phys. 16, 361 (1948).
[3] Steacie, Darwent, and Trost, Faraday Soc. Disc. 2, 80 (1947).
[4] J. R. Dingle and D. J. LeRoy, J. Chem. Phys. 18, 1632 (1950).

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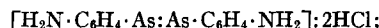[J. Chem. Phys. 19, 1051 (1951)]

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ON p. 1051, right-hand column, last line, "mean values" should read "mean value."

On p. 1052, left-hand column, 6th line below Table I, "characters" should read "character"; Table II,

$$[H_2N \cdot C_5H_4 \cdot As : As \cdot C_6H_4 NH_2] : 2HCl$$

should read

$$[H_2N \cdot C_6H_4 \cdot As : As \cdot C_6H_4 \cdot NH_2] : 2HCl;$$

and right-hand column, 1st line below Table I, for "alkyl arsines" should read "aryl arsines."

On p. 1054, caption for Figs. 1 and 2, omit the following words from the caption: "Fig. 1 (above). χ_m plotted against Z for several salts of As, Sb, and Bi" and "Fig. 2 (below) χ_m plotted against Z for the halides of As, Sb, and Bi"; right-hand column, 19th line from top, the equation should read $\chi : O = \chi - As : O(OH)_2 - \chi \equiv As(OH)_2$; and right-hand column, 12th line from bottom "magnitude 0.5λ" should read "magnitude $-5λ$."

On p. 1055, caption for Figs. 3 and 4, omit the following words from the caption: "Fig. 3 (above): χ_m plotted against Z for the oxides, sulfides, and iodides of As, Sb, and Bi." and "Fig. 4 (below): χ_m plotted against N for compounds containing the same anion."

On p. 1056, right-hand column, 22nd line from top, "χR" should read "Z_R."

Free Radical Processes in the Photolysis of Acetone

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THE mechanism for the photodecomposition of acetone in the vapor phase for the wavelength region 2000–3000A has been fairly well established,[1] but there have been differences of opinion and experimental finding concerning the region above 3000A. In particular there have been conflicting findings with regard to the nature of the primary process at the longer wavelengths. Several groups are inclined to the interpretation that the primary process above 3000A is predominantly direct dissociation into ethane and carbon monoxide.[2-4]

The nature of the primary process can be tested experimentally through a study of the photolysis of a mixture of C_2H_6CO and C_2D_6CO. A free radical mechanism should lead to 25 percent each of C_2H_6 and C_2D_6 and 50 percent $C_2H_3D_3$ in the ethane fraction.

A molecular mechanism will give none of the mixed ethane $C_2H_3D_3$. Thus from the amount of mixed ethane produced it would

be possible to calculate precisely the contribution of the two processes.

A sample of heavy acetone (>96 percent D) was prepared by successive exchanges of D_2O and light acetone. Fifty-percent mixtures of this material with C_2H_6CO were prepared in sealed quartz tubes and irradiated under the following conditions: at 2537A at 60°C and 120°C; at 3000–3400A at 35°C and 80°C.

The products after photolysis were fractionated, and the ethane samples analyzed with a mass spectrometer, using C_2H_6 and C_2D_6 samples for calibration.

It was found that the ethane distribution at all temperatures and wavelengths corresponded to within 2 percent of that predicted for a completely free radical mechanism. The conclusion is, therefore, that the primary process in the photolysis of acetone is a direct split into free radicals at all wavelengths. Further details of this work will appear in a subsequent article.

The authors wish to express their appreciation to Mr. Phillip Magee of the Chemistry Department for his aid in preparing the heavy acetone and to the Atomic Energy Commission for the sample of heavy water used. We are also indebted to Mr. Lake, Mr. Ellis, and Mr. Murrill of the Union Oil Research Group at Brea, California for conducting the mass spectrograph analysis.

1 L. M. Dorfman and W. A. Noyes, Jr., J. Chem. Phys. 16, 557 (1948); 16, 788 (1948).
2 R. Spence and W. Wild, J. Chem. Soc., 352 (1937).
3 Feldman, Burton, Ricci, and Davis, J. Chem. Phys. 13, 440 (1945).
4 Volman, Leighton, Blacet, and Brinton, J. Chem. Phys. 18, 203 (1950).

A Tentative Interpretation of the Magnetic Behavior of Pr6O11

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SHERMAN W. RABIDEAU[1] has measured the magnetic susceptibilities of three stable oxides of praseodymium, Pr_2O_3, Pr_6O_{11}, and PrO_2 over a temperature range between 80°K and 300°K. According to his experimental results, the susceptibilities of Pr_2O_3 and PrO_2 obey the Curie-Weiss law with negative paramagnetic Curie temperatures, whereas the reciprocal susceptibility vs temperature plot for Pr_6O_{11} manifests a curvature, not a straight line like the other two oxides, running across the temperature axis at a positive value, though this temperature was not reached in the above experiments. The effective Bohr magneton numbers for the three oxides are all in accordance with the values expected from the Hund's or Van Vleck and Frank's theory, considering Pr_6O_{11} as a mixture of Pr^{3+} and Pr^{4+} with the ratio of 1:2.

The negative paramagnetic Curie temperatures for the sesquioxide and dioxide show these two oxides to be antiferromagnetic materials, and therefore their magnetic susceptibilities would manifest a maximum value at each antiferromagnetic Curie temperature roughly corresponding to the absolute value of the paramagnetic Curie temperature. As for the case of Pr_6O_{11}, it is considered that its magnetic behavior can be interpreted on the basis of the model proposed by the writer for the interpretation of the magnetic properties of pyrrhotite.[2] This interpretation seems to be applicable to most materials in which a weak ferromagnetism appears as their chemical compositions deviate from those of the ideal stoichiometric materials which show the antiferromagnetism, such as FeS and αFe_2O_3.[3]

The x-ray analysis of these three oxides made by J. D. McCullough[4] showed that the crystal structure of Pr_2O_3 is hexagonal and those of Pr_6O_{11} and PrO_2 are both of the cubic fluorite type, and furthermore he concluded from the observed relative intensities of the diffraction lines that Pr_6O_{11} has a structure missing one-twelfth of the oxygen ions randomly from the oxygen lattice points of an ideal structure. Therefore, in Pr_6O_{11} vacant oxygen lattice points are distributed at random. Since PrO_2, having the same crystal structure as that of Pr_6O_{11}, is an antiferromagnetic substance, it will be divided into two sublattices, each having Pr ions with + or − magnetic moment alone below its antiferromagnetic Curie temperature, also Pr_6O_{11} will be divided into two such sublattices below its antiferromagnetic Curie point. Thus if Pr^{3+} ions and Pr^{4+} ions are uniformly distributed over two magnetic sublattices in the latter substance, it will only manifest the antiferromagnetism, and its magnetic susceptibility will obey the Curie-Weiss law above the Curie point. On the other hand, in the case that Pr^{3+} ions have a tendency to occupy only one of the two magnetic sublattices below the Curie temperature, the magnetic moments on the two sublattices will not completely compensate each other on account of the different magnetic moments carried by Pr^{3+} and Pr^{4+} ions, and therefore a spontaneous magnetization equal to the difference of the magnetizations on the two sublattices will appear. L. Néel[5] called such a ferromagnetism essentially originating in the antiferromagnetism, "ferrimagnetism."

If the second situation, that Pr^{3+} ions are preferably situated on one of the two magnetic sublattices, is taking place in Pr_6O_{11}, the ferromagnetism will appear below the antiferromagnetic Curie temperature, and therefore above the Curie point. The reciprocal susceptibility will deviate from the linear Curie-Weiss law holding at the higher temperature side as the temperature is lowered, having a curvature so as to pass through zero at the antiferromagnetic Curie point, because otherwise the susceptibility at the Curie point would remain a finite value.

The experimental susceptibility of Pr_6O_{11} shows just such a ferrimagnetic feature in the temperature range between which the experiments have been made. Therefore, it is expected that this substance will become ferromagnetic below the Curie temperature which is supposed probably not to be so much lower than 80°K, while PrO_2 will become only antiferromagnetic at about this temperature. However, such an interpretation of the magnetic properties of Pr_6O_{11} mentioned above will, in future, be ascertained by the experiments in the lower temperature region.

1 Sherman W. Rabideau, J. Chem. Phys. 19, 874 (1951).
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