sign conventions of C_1 and C_2. That is, they adopted the Lewis convention. They added, however, only C_2 could be called the *electrode potential*. I have no serious objection to this definition of electrode potential, although it is not really such, since the state of the electron is not defined. I would prefer to call C_1 the relative oxidation potential of Zn and C_2 the relative reduction potential of Zn^{++}. If anyone prefers to tabulate reduction potentials instead of oxidation potentials, he certainly has the right to do so, but it is ridiculous to claim that one is more fundamental than the other.

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A METHOD FOR THE STUDY OF CHLORINE ATOM REACTIONS. THE REACTION $Cl + CH_4 \rightarrow CH_3 + HCl$

Sir:

The reactions of chlorine with hydrogen and the hydrocarbons are chain reactions and as such their over-all rates are extraordinarily sensitive to the presence of traces of impurities, the condition of the reaction vessel and the intensity of the absorbed light in photochemical systems. Consequently, the many attempts which have been made to determine the rate constants of the elementary reactions of chlorine atoms, particularly those of type 1, have met with disproportionately little success.

$$Cl + RH = HCl + R \qquad (1)$$

However, the rate constant of the reaction 2 is known[1] to be given by $k_2 = 10^{13.9}$ exp. $(-5500 \pm 200/RT)$ moles^{-1} cc. sec.$^{-1}$. So that if the rate of

$$Cl + H_2 = HCl + H \qquad (2)$$

reaction 2 can be compared with that of reaction 1 in the same reaction system, k_1 may be found without having to make a direct estimate of chlorine atom concentrations: we have done this and determined k_1 for the reaction with methane in the following way.

Measured quantities of methane and hydrogen were sealed up in a 160 cc. Pyrex reaction vessel together with some 2.55×10^{-4} mole of chlorine, which is frozen out. The reaction is started by placing the vessel in a liquid or vapor bath which raises its temperature very rapidly. After a short interval to allow the vessel to attain the desired temperature, it is strongly illuminated. When a convenient period has elapsed the vessel is re-attached to a vacuum system and the residual hydrogen and methane separated from the products by low temperature distillations and adsorption in silica gel and measured.

The available evidence indicates that the hydrogen atoms and radicals formed will react with chlorine molecules for these reactions probably take place on every collision and hence the rate constants are approximately one hundred times those of any competing process, so that reactions 1 and 2 are the only ones by which methane and hydrogen are removed or formed. Then it can be readily shown[2] that if

$$-\,d[CH_4]/dt = k_1[CH_4]\,[Cl] \text{ and } -\,d[H_2]/dt = k_2[H_2][Cl]$$

then

$$k_1/k_2 = \log \{[CH_4]_i/[CH_4]_f\}/\log\{[H_2]_i/[H_2]_f\}$$

where the subscripts refer to the initial and final concentrations of the reactants. The reproducibility of k_1/k_2 for various ratios of methane to hydrogen is shown in the table. In Fig. 1 the logarithm of k_1/k_2 is plotted against $10^3/T$. The curvature of the points which is very small for a temperature range from 0° to 215° may be partially due to the effective temperature of the reaction being slightly below that of the bath at the higher temperatures. However, it seems that this can cause only a very small error in the slope of the line. It can be seen that the variation of k_1/k_2 with temperature is given by $k_1/k_2 = 10^{0.59}$ exp $(-1700/RT)$. Hence $k_1 = 10^{14.5}$ exp $(-3800/RT)$ mole^{-1} cc. sec.$^{-1}$.

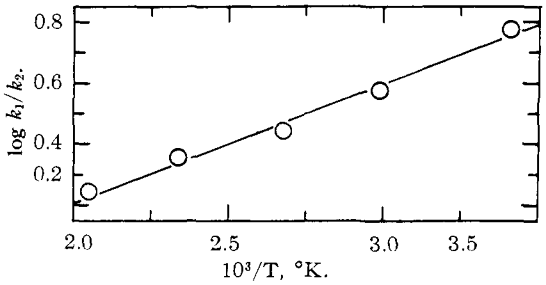

Fig. 1.

RUNS AT 100°

Initial concn., 10^{-7} mole cc.$^{-1}$ $[H_2]$	$[CH_4]$	Amount reacted, 10^{-7} mole cc.$^{-1}$ $\Delta[H_2]$	$\Delta[CH_4]$	k_1/k_2
28.34	27.96	2.22	6.96	2.76
35.98	44.81	2.75	8.98	2.81
58.15	52.19	4.72	7.54	3.01
66.57	33.80	5.27	6.46	2.57
76.77	33.27	5.24	7.72	2.88
81.34	51.16	4.09	8.62	2.79

Assuming that the standard entropy of the methyl radical is 45.5 e.u. and that the strength of the CH_3–H bond is 102.5 kcal./mole at 25°, we can make use of the approximate relation k = exp $(\Delta S°/R)$ exp $(-\Delta H°/RT)$ which neglects the small variations of ΔS and ΔH with temperature. Then we find for the equilibrium constant of reaction 1

$$K_1 = 10 \exp (1000/RT)$$

Therefore the rate constant, k_{-1}, of the reverse reaction is $k_{-1} = 10^{13.5}$ exp $(-4800/RT)$ mole^{-1} cc. sec.$^{-1}$ which is equal to $10^{11.0}$ mole^{-1} cc. sec.$^{-1}$ at 150°. At this temperature Cvetanović and Steacie[3] find $k_{-1} = 10^{10.4}$ mole^{-1} cc. sec.$^{-1}$; although they report an activation energy of only 2.3 kcal./mole for reaction (−1). However, their activation energy is based on points at 25° and 150° only and it is known that the study of the reactions of methyl radicals derived from the photol-

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[1] P. G. Ashmore and J. Chanmugam, *Trans. Faraday Soc.*, **49**, 254 (1953).

[2] W. M. Jones, *J. Chem. Phys.*, **19**, 78 (1951).

[3] R. J. Cvetanović and E. W. R. Steacie, *Can. J. Chem.*, **31**, 158 (1953).

ysis of acetone at low temperatures tends to yield low values for the activation energies.[4]

With slight modifications this method can be adapted to the study of many other chlorine atom reactions. The results will be reported in full when the program of work is complete.

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RECEIVED NOVEMBER 30, 1953

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(4) A. J. C. Nicholson, THIS JOURNAL, **73**, 3981 (1951).

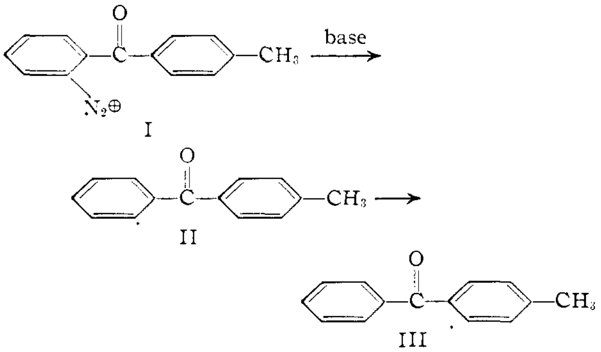
(5) E. I. du Pont de Nemours & Co., Niagara Falls, N. Y.

A NEW TYPE OF CHAIN TRANSFER REACTION[1]

Sir:

In the course of studies on the intramolecular reactions of free radical intermediates we have been investigating the reactions of diazotized 2′-amino-4-methylbenzophenone (I). Evidence has already been presented[2] which indicates that the C–N cleavage of the diazonium group can occur by either a heterolytic or by a homolytic process, the former under acidic conditions, the latter under alkaline conditions.

We have been successful in obtaining evidence for the intramolecular chain transfer step (II → III)



I

II

III

and believe this to be the first actual demonstration of this type of reaction between an aryl radical and an aromatic ring. Decomposition of a stirred mixture of the diazonium fluoborate (I), carbon tetrachloride and sodium hydroxide led to a complex reaction mixture from which could be isolated by chromatography an oily fraction containing 3-methylfluorenone (10% based on the diazonium salt), 2′-chloro-4-methylbenzophenone (10%) and 2-chloro-4-methylbenzophenone (10%). The last named product is the one expected from reaction of the radical III with carbon tetrachloride. The products were identified and determined quantitatively by means of the infrared spectra of solutions in carbon disulfide. The melting points and the analytical infrared peaks of the model compounds were as follows: 3-methylfluorenone[3] 66.0–66.5° (10.88, 9.02), 2′-chloro-4-methylbenzophenone[4] 98.5–99.5° (10.78, 13.43), 2-chloro-4-methylbenzophenone 51.0–52.0° (10.69, 12.20).

We have applied this technique to several other reactions with most encouraging results. As reported elsewhere[2] the reaction of the diazonium salt I in aqueous sodium chloride under acidic conditions leads to a mixture of 2′-hydroxy-4-methylbenzophenone (21%), 2′-chloro-4-methylbenzophenone (14%) and 3-methylfluorenone (60%). This heterolytic reaction is not expected to lead to any of the "wrong" 2-chloro-4-methylbenzophenone, and we found this "wrong" chloro compound was absent within the experimental error (no 10.69 peak). Similarly with sodium bromide the expected 2′-bromo-4-methylbenzophenone was the only halogen-containing compound found (no 10.71 peak). In contrast to the above reactions, the Sandmeyer reaction of I with cuprous bromide gives a mixture of 2′-dromo-4 methylbenzophenone and 2-bromo-4-methylbenzophenone. This seems to be a clear demonstration that this Sandmeyer reaction proceeds at least in part by a free radical mechanism in which the radical is free enough to undergo the chain transfer step II → III. The melting points and the analytical infrared peaks of the model compounds were as follows: 2′-bromo-4-methylbenzophenone[5] 89.0–90.0° (10.79); 2-bromo-4-methylbenzophenone, b.p. 171–172° (3 mm.) (10.71). Reaction of the diazonium salt I with sodium iodide in aqueous solution proceeded as follows: at a *p*H of 1 and of 7 (phosphate) only one iodo compound was produced, 2′-iodo-4-methylbenzophenone; m.p. of model compound 52–53° (10.80). At a *p*H of 11 the yield of iodo compounds was smaller, but both the 2′,4- and the 2,4-isomers appear to be present since the infrared spectra had peaks at 10.69, 10.80 and 10.88 μ. The spectra of a series of benzophenones indicates that a 10.70 peak is characteristic of the benzoyl group and a 10.80 peak is characteristic of the *p*-toluyl group.

These results are of some importance in planning the use of the Sandmeyer and related reactions for synthetic purposes. We expect the reactions to be of great help in a study of several of the diazonium salt reactions and in a study of free radical reactions.

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(1) Supported by a Rohm & Haas research assistantship (DIR) and by a National Science Foundation Grant.

(2) D. F. DeTar and S. V. Sagmanli, THIS JOURNAL, **72**, 965 (1950); D. F. DeTar and D. I. Relyea, THIS JOURNAL, in press.

(3) F. Ullmann, *Ber.*, **31**, 1694 (1898).

(4) W. D. Cohen, *Rec. trav. chim.*, **38**, 117 (1918).

(5) A. Heidenreich, *Ber.*, **27**, 1452 (1894).

A NEW METHOD FOR DETERMINING ADSORPTION SEPARATION FACTORS AND ADSORBENT CAPACITIES

Sir:

In a recent publication[1] we reported an equation for determining adsorption separation factors of liquids in static systems. Use of the equation as given there is only possible if the adsorbent capacities are determined by some independent method, and if these values are assumed to equal the "selective" adsorbent capacities.

In more recent studies we have found that the selective adsorbent capacity need not be deter-

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(1) R. W. Schiessler and C. N. Rowe, THIS JOURNAL, **75**, 4611 (1953).