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.

H. O. PRITCHARD
THE UNIVERSITY J. B. PYKE
MANCHESTER, ENGLAND A. F. TROTMAN-DICKENSON[5]

RECEIVED NOVEMBER 30, 1953

---

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

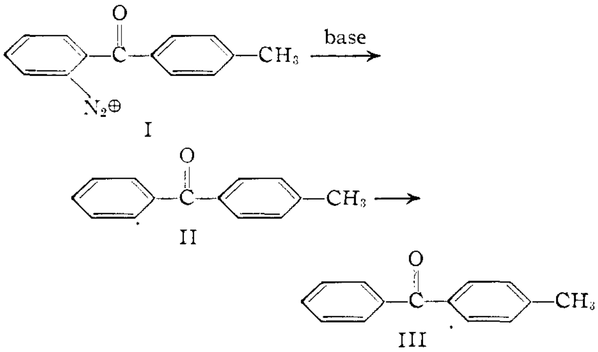
(5) E. I. du Pont de Nemours & Co., Niagara Falls, N. Y.

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)



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.

---

(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).

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF SOUTH CAROLINA DOUGLAS I. RELYEA
COLUMBIA, SOUTH CAROLINA DELOS F. DETAR

RECEIVED JANUARY 15, 1954

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-

---

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

mined independently, but that both the separation factor and the true selective adsorbent capacity may be determined simultaneously from the experimental data for static liquid–adsorbent systems.

The reported expression[1,2]

$$\alpha - 1 = \frac{(V^{i}_{A} - V^{1}_{A})X}{V^{1}_{A}\,[V^{1}_{B}\,Wz - (V^{i}_{A} - V^{1}_{A})X]} \qquad (1)$$

may be transformed into the form of an equation for a straight line by taking the reciprocal of both sides, and rearranging

$$V^{1}_{A} = \frac{V^{1}_{A}V^{1}_{B}\,W}{(V^{i}_{A} - V^{1}_{A})X}\,z - \frac{1}{\alpha - 1} \qquad (2)$$

A second equation of a straight line is obtained by dividing equation 2 by $V^{1}_{A}V^{1}_{B}W/(V^{i}_{A} - V^{1}_{A})X$

$$\frac{(V^{i}_{A} - V^{1}_{A})X}{V^{1}_{B}\,W} = -\frac{(V^{i}_{A} - V^{1}_{A})X}{V^{1}_{A}V^{1}_{B}\,W}\left(\frac{1}{\alpha - 1}\right) + z \qquad (3)$$

If the separation factor, α, and the selective adsorbent capacity, z, are constant with varying initial liquid compositions, then plots $V$of ${}^{1}_{A}$ *vs.* $V^{1}_{A}V^{1}_{B}W/(V^{i}_{A} - V^{1}_{A})X$ and $(V^{i}_{A} - V^{1}_{A})X/V^{1}_{B}W$ *vs.* $(V^{i}_{A} - V^{1}_{A})X/V^{1}_{A}V^{1}_{B}W$ will give straight lines from which the separation factor and the selective adsorbent capacity may be determined from the slope or the intercept, depending on the equation used.

The equations were tested experimentally using binary mixtures of several pure hydrocarbons in static systems. For each binary used several compositions were employed, using only 1 to 2 g. of adsorbent and 1 to 2 cc. of liquid mixture. The compositions were determined by refractive index, using a refractometer with a precision of ±0.00005 and an experimental refractive index–composition diagram. Both activated alumina (Alcoa, F-20) and silica gel (Davison, 28-200 Mesh) were employed as adsorbents.

An example of the constancy of the separation factor and the adsorbent capacity is illustrated in Fig. 1 in which the data for toluene–*n*-heptane mixtures on alumina are plotted. Deviation from linearity at higher concentrations of toluene is within the limits of precision. Equation 3 is less reliable due to increased sensitivity. In Fig. 1, the values obtained for the separation factor and the selective adsorbent capacity are 7.70 ± 0.67 and 0.062 ± 0.003 cc./g., respectively.

The results for the separation of low molecular weight hydrocarbon pairs on alumina and silica gel strongly indicate that the method is an improvement over previous attempts[1,3] to define and determine the true selective adsorbent capacity of the adsorbents for the liquids presented to them. The separation factors found are constant with composition, a fact not revealed by previous methods, and these separation factors should be the true values since only initial and equilibria data are needed.

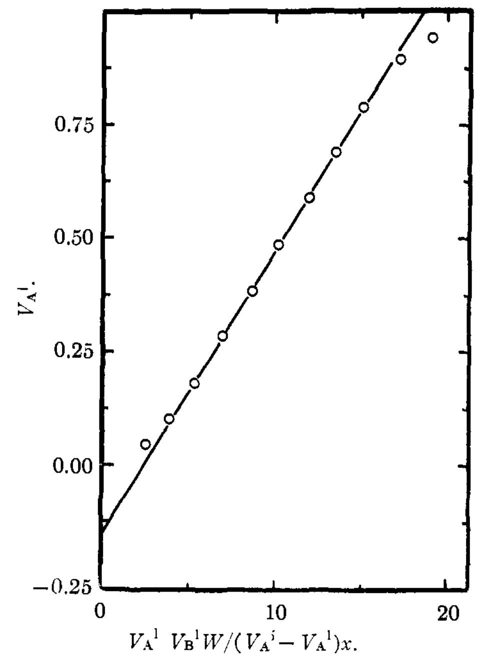


Fig. 1.—Results of equation 2 with *n*-heptane–toluene mixtures on activated alumina.

The detailed results for adsorbents and liquid binaries already examined will be the subject of a separate publication. The investigation is being continued.

AMERICAN PETROLEUM INSTITUTE
RESEARCH PROJECT 42, WHITMORE LABORATORY
COLLEGE OF CHEMISTRY AND PHYSICS CARLETON N. ROWE
THE PENNSYLVANIA STATE UNIVERSITY
STATE COLLEGE, PENNA. ROBERT W. SCHIESSLER

RECEIVED DECEMBER 19, 1953

---

[2] α = adsorption separation factor
A = component preferentially adsorbed
V^{i}_{A} = vol. fctn. of A in original liq. mixt.
V^{1}_{A} = vol. fctn. of A in liq. phase at equil. $V^{1}_{B} = 1 - V^{1}_{A}$
X = vol. of original liq. mixt. in cc.
W = weight of adsorbent
z = selective capacity of adsorbent, cc./g.

[3] B. J. Mair, J. W. Westhaver and F. D. Rossini. *Ind. Eng. Chem.*, **42**, 1279 (1950).

THE PREPARATION OF STANNANE

Sir:

In the course of an investigation of the reduction of tin in acid solution with aqueous sodium borohydride, an unexpectedly large quantity of stannane was obtained. On the basis of the behavior of elements in the neighboring groups toward this reagent, it was expected that the reduction product would be principally metallic tin, with the possibility of a small amount of the hydride. Instead, yields of stannane as high as 84% were obtained from the borohydride reduction of tin(II) chloride in 0.6 *N* hydrochloric acid solution.

The only efficient method of preparation of stannane heretofore available was the reduction of tin(IV) chloride in ether by means of lithium aluminum hydride.[1] Those methods of preparation involving reduction of tin salts in aqueous solution by metals or metal alloys[2] or electrolytic

---

[1] A. E. Finholt, A. C. Bond, Jr., K. E. Wilzbach and H. I. Schlesinger, THIS JOURNAL, **69**, 2692 (1947).

[2] F. Paneth and K. Fürth, *Ber.*, **52**, 2020 (1919); F. Paneth, A. Johannsen and M. Matthies, *ibid.*, **55**, 769 (1922); I. Alimarin and Arest-Yakubovich, *C.A.*, **31**, 6573 (1937).