tion of pure triphenylchloromethane in neutral absolute ethyl alcohol to stand at room temperature overnight. The solvent was evaporated under reduced pressure in a desiccator which contained fused calcium chloride. Samples of the dried residue melted at 81–82° and the melting point of mixtures of this residue and the purified ether, which was prepared as first described, showed that the residue was practically pure ethyl ether of triphenylcarbinol.

The absolute ethyl alcohol which was used as solvent was obtained by a careful fractionation of 99.5% ethyl alcohol which had been distilled from anhydrous potassium hydroxide. A two centimeter layer of the liquid was perfectly transparent at all frequencies within the limit of our equipment. The ether that was used as solvent was in most cases a product obtained on the market as "Reagent Ether Anhydrous." This ether, without further purification, was optically clear and was without effect upon the solute; however, for some of the work, it was distilled from fresh metallic sodium.

Summary

1.   Curves are presented which show the quantitative absorption spectra in the ultraviolet of ether solutions of triphenylmethane, triphenylcarbinol, triphenylchloromethane and the ethyl ether of triphenylcarbinol; also curves which show the absorption of absolute ethyl alcohol solutions of benzophenone and the ethyl ether of triphenylcarbinol.

2.   It has been shown that the curve obtained from a solution of triphenylchloromomethane in neutral absolute ethyl alcohol is in reality the absorption curve of the alcohol solution of the ethyl ether of triphenylcarbinol.

ANN ARBOR, MICHIGAN

THE REACTION OF ISOPROPYL IODIDE WITH MERCURIC CHLORIDE

BY BEN H. NICOLET AND WILLIAM MCDANIEL POTTS[1]

Conant and others[2] have recently studied the reaction RCl + KI = RI + KCl (R representing a considerable variety of alkyl and other radicals) in some detail. With the simpler alkyl chlorides, it took place some 60 times more rapidly for primary than for secondary chlorides. They found the reaction quite strictly of the second order, and so slightly reversible that the opposing reaction (if any) did not need to be considered in the calculation of velocity constants.

Nevertheless, Oppenheim[3] in 1860 reported that ethyl chloride and amyl chloride could be obtained by the action of mercuric chloride on the

[1] The material here presented was used by William McDaniel Potts in partial satisfaction of the requirements for the degree of Master of Science, at the University of Chicago, 1927.

[2] (a) Conant and Kirner, THIS JOURNAL, 46, 352 (1924); (b) Conant and Hussey, ibid., 47, 476 (1925); (c) Conant, Kirner and Hussey, ibid., 47, 488 (1925).

[3] Oppenheim, Ann., 140, 207 (1860).

respective iodides. By a similar process, Maumene[4] made $ClCH_2CH_2I$ and $C_2H_4Cl_2$ from $C_2H_4I_2$. Later, Linnemann[5] prepared butyl chloride in 70% yield by the action of mercuric chloride on butyl iodide at 120–130°.

This reaction[6] thus has the appearance of being an effective reversal of the conversion of chlorides to iodides as studied by Conant and his collaborators. Such a reversal might be explained as due to the fact that the concentration of iodide ion in mercuric iodide solutions is excessively small, even in comparison with the chloride-ion concentration in solutions of mercuric chloride.

On the grounds suggested, the reaction of *iso*propyl iodide with mercuric chloride in dry ether was studied, and found to take place at a rate proportional to the concentrations of these two substances, and also to the concentration of the mercuric iodide. In the calculation of velocity constants, it was found possible to neglect the reverse reaction. *Iso*-propyl iodide was chosen after it had been found that *n*-propyl iodide reacted at least 50 times more slowly. This ratio again favors the idea that the reaction is really a reversal of that studied by Conant.

Experimental Part

Choice of a Solvent.—It has already been shown[7] that alcohol is not a suitable solvent for the study contemplated, as in it the chief reaction would be one of alcoholysis, catalyzed by the mercuric halide. A suitable solvent would be one which did not react with mercuric salts, which contained no hydroxyl group and which dissolved mercuric iodide to a considerable extent. As the simplest compromise, absolute ether was selected, although it dissolved so little mercuric iodide that, at convenient concentrations of the reacting substances, it was possible to follow the reaction only to 25–50% completion; beyond this, mercuric iodide separated.

Procedure.—The reacting substances were dissolved in absolute ether in the desired proportions, the solution was made up to 200 cc. and the whole kept in a thermostat at 25°. Samples of 10 cc. were withdrawn at suitable intervals and analyzed for inorganic iodine as follows:

The sample was placed in a 150cc. flask and dry air drawn through until the ether and organic iodide were completely evaporated. Blank determinations showed that less than 0.5% of the organically combined iodine was converted to mercuric iodide under these conditions. The dry residue was covered with water, made acid with sul-

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[4] Maumene, *Jahresb. über die Fortschritte der Chem.*, **1869**, p. 345.

[5] Linnemann, *Ann.*, **161**, 197 (1872).

[6] We have also found that when solid mercuric chloride is covered with a moderate excess of ethyl iodide in a closed flask, which is allowed to stand for some days, remarkably good crystals of mercuric iodide separate. This is, in fact, an excellent method of growing such crystals. It might be predicted that *iso*propyl iodide would give more rapid results, but it is not clear whether this would be an advantage in the formation of such crystals.

[7] Nicolet and Stevens, THIS JOURNAL, **50**, 135 (1928).

furic acid and mossy zinc added.   The solution was allowed to stand until the mercury was completely precipitated.   The iodine was then liberated with nitrosylsulfuric acid, extracted with carbon disulfide, and the extract titrated with standard thiosulfate solution.

Typical results are given in Table I.   At all the concentrations listed, mercuric iodide was still completely dissolved.   Each run was discontinued when the iodide began to separate.

<div align="center">TABLE I</div>

REACTION OF MERCURIC CHLORIDE WITH *Iso*PROPYL IODIDE IN ETHER AT 25°

Case A: Mercuric chloride, 0.1425 M; *iso*propyl iodide, 0.285 M

Expt. no.	Time, hrs.	*Iso*propyl iodide transformed, moles	K
1	70	0.0194	
			0.56[a]
2	118	.0305	
			.57
3	169	.0475	
			.58
4	215	.0668	
			Av. .57

Case B: Mercuric chloride, 0.1425 M; *iso*propyl iodide 0.1425 M

1	92	0.0113	
			0.77[b]
2	236	.0283	
			.68
3	308	.0395	
			.83
4	355	.0497	
			.70
5	404	.0592	
			.82
6	452	.0700	
			Av. .76

Case C: Mercuric chloride, 0.0712 M; *iso*propyl iodide, 0.1425 M; mercuric iodide (initial), 0.0185 M

|			
1	19	0.00162	0.45[c]
2	93	.0064	.35
3	141	.0107	.38
4	187	.0157	.41
5	284	.0276	.47
6	309	.0299	.47
			Av. .44

[a] Values for Case A calcd. for successive intervals from Equation 2.

[b] Values for Case B calcd. for successive intervals from Equation 1.

[c] Values for Case C calcd. from Equation 3.

Calculation of Velocity Constants

The reaction is obviously autocatalytic. In the equation

$$HgCl_2 + 2(CH_3)_2CHI = HgI_2 + 2(CH_3)_2CHCl$$
$$\quad (a) \qquad\qquad (b) \qquad\qquad (d)$$
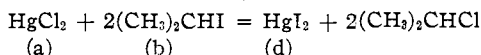
the initial concentration of each substance present may be represented by the letter beneath its formula. The values of K in Table I were calculated, for Case B, from the formula

$$\frac{dx}{dt} = \frac{K}{4}(2a - x)(b - x)x \tag{1}$$

It is apparent that, at the time t, the concentrations of mercuric chloride and iodide may be represented by $(2a - x)/2$ and $x/2$, respectively, x representing moles of iodide transformed. For Case A (in which $2a = b$), this becomes

$$\frac{dx}{dt} = \frac{K}{4}(b - x)^2 x \tag{2}$$

Finally, in Case C, mercuric iodide was added at the beginning to confirm the assumption that it was responsible for the catalytic effect observed. As for simplicity concentrations were so chosen that $2a = b$, the corresponding equation was

$$\frac{dx}{dt} = \frac{K}{4}(b - x)^2(2d + x) \tag{3}$$

A possible interpretation of the reaction mechanism which would be consistent with the equations used would be the following. *Iso*propyl iodide reacts extremely slowly with mercuric chloride, but with mercuric iodide it forms a complex $(CH_3)_2CHI \cdot HgI_2$ which reacts (in the molecular ratio 1:1) with mercuric chloride (or perhaps with chloride ion) at a considerably greater rate. This complex is relatively rapidly formed in reversible reaction, so that its concentration (probably small) is proportional to $x(b - x)/2$.

Discussion of Results

In Cases A and B, the nature of the integrated equation requires that the constants be calculated between intervals and not from zero time. To save space in presentation, these calculations have been made between *successive* intervals, which magnifies the errors of individual determinations. The values of K are, however, sufficiently consistent in each series to indicate agreement with the type of equation used. The variation in the average values for the different series still requires explanation.

While the data presented give a fairly satisfactory account of the reaction under discussion, there is a definite logical defect in the equations used in the calculations given. It is not strictly possible that the entire reaction velocity should be proportional to the concentration of a product of the reaction not initially present.

It must be assumed, therefore, that the observed velocity is really made up of the sum of the velocity represented in accordance with the equations used and the velocity of the (evidently much slower) reaction of *iso*propyl iodide with mercuric chloride alone. Using the same symbols as before, the true equation would probably have one of the following forms

$$\frac{dx}{dt} = \frac{K}{4} (2a - x) (b - x)x + \frac{K'}{2} (2a - x) (b - x) \tag{4}$$

$$\frac{dx}{dt} = \frac{K}{4} (2a - x) (b - x)x + \frac{K'}{4} (2a - x)^2(b - x) \tag{5}$$

In Equation 4, the slow reaction is represented as being the simplest possible. Equation 5 represents the assumption that the slow reaction is catalyzed by mercuric chloride in the same way that the main reaction is catalyzed by mercuric iodide.

Calculations of constants based on both these equations have been made but, as might have been expected from the figures already presented, the "slow component" of the reaction is so very slow, and makes such a slight contribution to the total "K," that a decision between the mechanisms suggested in these two equations would be quite impossible with the present data.

Further work is planned to determine more definitely whether the present reaction actually constitutes a true reversal of the reaction studied by Conant. If it does, there is every reason to believe that the latter reaction should also be powerfully catalyzed by mercuric iodide. It is apparent that this test cannot be applied experimentally, since the catalyst (HgI_2) is incompatible with one of the reactants (iodide ion). While obviously no contradiction is here involved, the apparent paradox is interesting.

Summary

1. The reaction of *iso*propyl iodide (and presumably of other iodides) with mercuric chloride (measured in ether at 25°) takes place at a rate proportional to the product of the concentrations of these two substances and of the mercuric iodide formed. The reaction evidently goes practically to completion.

2. This reaction is pictured as a reversal of that of alkyl (and other) chlorides with iodide ion. which also goes practically to completion.

CHICAGO, ILLINOIS