[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, RUTGERS UNIVERSITY]

Studies on the Pinacol Rearrangement. II. A Kinetic Study of Some Reactions of 1,1,2-Triphenyl-2-bromoethanol

BY JOHN F. LANE AND DAVID R. WALTERS[1]

This paper presents the results of a kinetic study of the reactions of 1,1,2-triphenyl-2-bromoethanol (I) in aqueous dioxane in the presence and absence of basic reagents. It is shown that the reactions of I with bases follow the kinetic law: $x' = k(a - x)(b - x)/(c + x)$ where a, b and c are, respectively, the initial concentrations of base, I and acid conjugate to the base, and x is the concentration of bromide ion at time t. In the absence of bases I undergoes a first-order solvolysis which leads to the mixtures of products described in Part I of this series. From the rates and compositions of products it has been possible to calculate thermodynamic quantities of activation which show that the order of participation for neighboring groups in this system is C_β-O$^-$ $\gg C_\beta$-Ph > C_β-OH.

In the preceding paper of this series[2] it was shown that 1,1,2-triphenyl-2-bromoethanol (I) in aqueous dioxane reacted with bases to produce triphenylethylene oxide (II) and with water alone to give mixtures containing predominantly phenyl benzhydryl ketone (III) with small amounts of triphenylethylene glycol (IV). Kinetic studies on the two types of reaction are presented here.

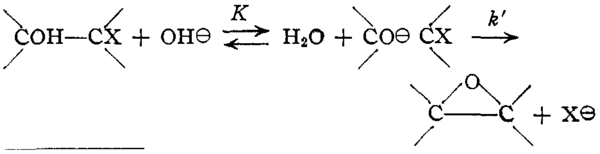
Measurement of Rates

All measurements of rates were conducted in a thermostated bath in which the temperature was held constant to 0.01°. A weighed sample of I was introduced into a volumetric flask in the bath, which was then filled with the desired medium, this solution having previously been brought to the correct temperature. The mixture was stirred for thirty seconds without removing the flask from the bath. Aliquot portions of the solution were then removed at suitable intervals. In reactions involving bases these were delivered into an excess of 0.05 *N* nitric acid to quench the reaction. The resulting solutions were extracted twice with chloroform. The bromide ion in the aqueous layer was then determined by the method of Volhard. In general, between five and ten aliquots were so determined in any given run.

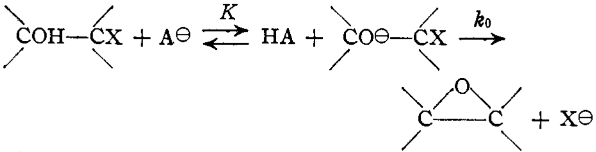
The dioxane used in these experiments was purified by the method of Eigenberger[3] and freshly distilled from sodium before use. The *p*-nitrophenol was the Eastman Kodak Co. White Label product recrystallized from alcohol. When the desired medium was a buffer solution of the phenol and its salt, the latter was prepared in the solution by addition of the calculated quantity of sodium hydroxide.

Discussion

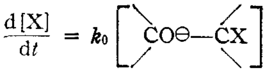
Reaction with Bases.—Previous kinetic studies on halohydrins[4] have shown that their reaction with hydroxide ion is bimolecular. For this reaction Lucas and Winstein[5] have proposed the mechanism



where the first step is a rapid reversible proton transfer and the second, the unimolecular, rate-determining decomposition of the ion of the halohydrin. For weaker bases, such as those used here, this becomes

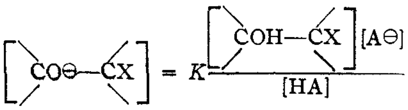


Since



$$\frac{d[X]}{dt} = k_0\left[>CO^{\ominus}-CX<\right]$$

and, since



$$\left[>CO^{\ominus}-CX<\right] = K\frac{\left[>COH-CX<\right][A^{\ominus}]}{[HA]}$$

the rate of production of halide ion is given by

$$\frac{dx}{dt} = k_0K\frac{(a-x)(b-x)}{x}$$

where a is the initial concentration of the base $A^{\ominus}$ and b, the initial concentration of the halohydrin; K, the equilibrium constant of the reversible proton transfer, is equal to K_A/K_{HA} where K_A is the dissociation constant of the halohydrin and K_{HA} that of the acid conjugate to $A^{\ominus}$.

Values of the experimental rate constant $k = k_0K$, are conveniently calculated by the relation $k = a\bar{k}_2 - \bar{k}_1$

$$\bar{k}_2 = \frac{2.303}{t(a-b)}\log\frac{b(a-x)}{a(b-x)};\ \bar{k}_1 = \frac{2.303}{t}\log\frac{b}{(b-x)}$$

When the acid is initially present in appreciable concentrations c this relationship of course becomes $k = (a + c)\bar{k}_2 - \bar{k}_1$. These values are reported in Table I for experiments involving acetate ion and buffer solutions containing *p*-nitrophenol and *p*-nitrophenolate ion. Data on typical calculations appear in Tables II and III.

The validity of the proposed mechanism is satisfactorily confirmed by the invariance of k under experimental conditions involving different concentrations of bromohydrin, base and conjugate acid. Moreover, the ratio of rates obtained with the two bases, acetate and *p*-nitrophenolate ion, is in reasonable agreement with the ratio of their basic strengths so far as this is known. The mechanism requires that

$$k_{(OAc^-)}/k_{(p\text{-}NO_2C_6H_4O^-)} = K_{(p\text{-}NO_2C_6H_4OH)}/K_{(HOAc)}$$

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[1] du Pont Fellow in Chemistry, Rutgers University, 1946–1948.

[2] John F. Lane and David R. Walters, THIS JOURNAL, **73**, 4234 (1951).

[3] E. Eigenberger, *J. prakt. Chem.*, [2] **130**, 75 (1931).

[4] J. E. Stevens, C. L. McCabe and J. C. Warner, THIS JOURNAL, **70**, 2449 (1948); C. L. McCabe and J. C. Warner, *ibid.*, **70**, 4031 (1948); L. Smith, *Z. physik. Chem.*, **156A**, 135 (1933).

[5] S. Winstein and A. J. Lucas, THIS JOURNAL, **61**, 1576 (1939).

TABLE I

VELOCITIES OF REACTIONS BETWEEN 1,1,2-TRIPHENYL-2-BROMOETHANOL (I) AND BASES IN 70% (AQUEOUS) DIOXANE

Experiment	Base	Initial concentrations (moles/l.) I	Base	Conjugate acid	Temp., °C.	Ionic strength	10^4k (min.$^{-1}$)
1	OAc^-	0.01954	0.2840	....	24.8	0.284	0.23 ± 0.00
2	OAc^-	.01954	.2840	....	24.8	.284	0.22 ± 0.01
3	OAc^-	.0189	.1454	....	40.0	.288[a]	2.60 ± .07
4	OAc^-	.0181	.1945	....	40.0	.288[a]	2.62 ± .05
5	OAc^-	.0171	.2819	....	40.0	.288[a]	2.47 ± .03
6	p-$NO_2C_6H_4O^-$	.02084	.1891	0.1949	24.8	.189	75.2 ± .3
7	p-$NO_2C_6H_4O^-$	.02077	.1891	.1949	24.8	.285[a]	71.3 ± .4
8	p-$NO_2C_6H_4O^-$	.02087	.1891	.1949	24.8	.285[a]	71.5 ± .4
9	p-$NO_2C_6H_4O^-$	.01688	.2810	.1030	24.8	.281	72.1 ± .8
10	p-$NO_2C_6H_4O^-$	.01736	.2814	.1026	24.8	.281	70.3 ± 1.2
						(Mean 7–10)	71.3 ± 0.5

[a] Ionic strength adjusted by the addition of sodium perchlorate.

TABLE II

RATE CONSTANT FOR THE REACTION BETWEEN 1,1,2-TRIPHENYL-2-BROMOETHANOL (I) (0.01810 *M*) AND SODIUM ACETATE (0.195 *M*) IN 70% (AQUEOUS) DIOXANE AT 40.0°

Time, min.	Bromide ion M	$(a + c)\bar{k}_2$	$\bar{k}_1$	10^4k (min.$^{-1}$)
0	0.00546			
15	.00751	0.008286	0.008036	2.50
30	.00892	.007344	.000775	2.69
50	.01033	.006536	.006271	2.65
75	.01173	.005938	.005680	2.58
105	.01306	.005454	.005188	2.66
135	.01414	.005102	.004840	2.62
7200	.02355			
			(Mean)	2.62 ± 0.06

TABLE III

RATE CONSTANT FOR THE REACTION BETWEEN 1,1,2-TRIPHENYL-2-BROMOETHANOL (I) (0.02077 *M*), SODIUM *p*-NITROPHENOLATE (0.1891 *M*) AND *p*-NITROPHENOL (0.1949 *M*) IN 70% (AQUEOUS) DIOXANE AT 24.8°

Time, min.	Bromide ion	$(a + c)\bar{k}_2$	$\bar{k}_1$	$10^3 k$ (min.$^{-1}$)
0	0.00289			
14	.00479	0.01399	0.00686	7.13
29	.00658	.01384	.00674	7.10
44	.00823	.01392	.00676	7.16
59	.00962	.01374	.00664	7.10
74	.01099	.01389	.00688	7.21
89	.01200	.01354	.00649	7.05
4000	.02366			
			(Mean)	7.13 ± 0.04

Since it may be assumed that the right-hand ratio is not much altered by changes in ionic strength and dielectric constant, it follows that

$$K_{(p\text{-}NO_2C_6H_6OH)} = 1.85 \times 10^{-5} \times k_{(OAc)}/k_{(p\text{-}NO_2C_6H_4O^-)}$$
$$= 5.77 \times 10^{-8} \text{ (in water at 25°)}$$

This value for the ionization constant of *p*-nitrophenol compares favorably with the values 9.6×10^{-8} [6] and 7.0×10^{-8} [7] reported elsewhere.

The specific rate of reaction of the bromohydrin with any base ($A^{\ominus}$) will be given by

$$k = (k_0K_A)/K_{HA} = 4.2 \times 10^{-10}/K_{HA}$$

Thus, the action of even a moderately weak base ($K_{HA} \sim 10^{-5}$) will cause epoxide formation at a measureable rate, while hydroxide ion ($K_{HA} \sim 1.1 \times 10^{-14}$) in moderate concentration will cause practically instantaneous conversion to the epoxide.

An approximate evaluation of k_0 (at 25°) may be obtained by estimating the pK_A for the bromohydrin by the method of Branch and Calvin[8] and employing the relation

$$k_0 = kK_{HA}/K_A$$

This gives

$$pK_A = 18.0 - 1.1(2_\alpha Ph) - 0.2(_\beta Ph) - 1.0(_\beta Br) = 15.7$$
$$k_0 = 2.25 \times 10^{-5} \times 1.85 \times 10^{-5}/2.0 \times 10^{-16} = 2.1 \times 10^6 \text{ (min.}^{-1}\text{)}$$

Solvolysis.—Values of the first-order constants for solvolysis of the bromohydrin in aqueous di-

TABLE IV

RATE CONSTANTS FOR THE ACTION OF AQUEOUS DIOXANE ON I

Experiment	Medium	Temp., °C.	Concn. of I	10^4k (min.$^{-1}$)
1	70% dioxane	40.0	0.0225	0.75 ± 0.02
2	70% dioxane	40.0	.0225[a]	1.29 ± 0.03
3	70% dioxane	50.0	.0231	2.73 ± 0.11
4	70% dioxane	50.0	.0231	2.69 ± 0.07
5	70% dioxane	70.0	.0213	31.1 ± 0.3
6	70% dioxane	70.0	.0213	31.4 ± 0.3
7	60% dioxane	40.1	.0238	2.04 ± 0.04
8	60% dioxane	40.1	.0238	2.14 ± 0.06
9	60% dioxane	40.1	.0238	2.08 ± 0.05
10	60% dioxane	50.1	.0222	8.58 ± 0.17
11	60% dioxane	49.9	.0234[b]	14.9 ± 0.9

[a] Solution was 0.2880 *M* in sodium perchlorate. [b] Solution was 0.6 *M* in sodium perchlorate.

TABLE V

RATE CONSTANT FOR THE ACTION OF 70% (AQUEOUS) DIOXANE ON 1,1,2-TRIPHENYL-2-BROMOETHANOL (I) (0.02133 *M*) AT 70.0°

Time, min.	Bromide ion M	$10^3 k_1$, min.$^{-1}$
0	0.00222	
30	.00417	3.18
75	.00663	3.09
105	.00815	3.10
220	.01286	3.14
285	.01492	3.17
345	.01641	3.17
2600	.02355	
	(Mean)	3.14 ± 0.03

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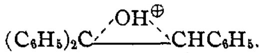
(6) A. Hantzsch, *Ber.*, **32**, 3066 (1899).

(7) H. Lunden, *J. chim. phys.*, **5**, 574 (1908); *cf. C. A.*, **2**, 1088 (1908).

(8) G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentiss-Hall, Inc., New York, N. Y., Chapter IV.

oxane are given in Table IV. Data on a typical determination are given in Table V. Like other solvolyses of the type S_N1, this is accelerated by an increase in the ionizing power of the medium. As pointed out in the preceding paper[2] of this series it may be considered as a composite of two processes, one leading to rearrangement through the intermediate (**B**)  $C_6H_5(OH)C\overset{Ph^{\oplus}}{\text{———}}CHC_6H_5$ and the other to glycol formation either by direct reaction with the solvent or *via* the intermediate (**C**)  $(C_6H_5)_2C\overset{OH^{\oplus}}{\text{———}}CHC_6H_5$.

The values given in Table IV, examined in the light of the previous discussion of the magnitude of the reaction of I with bases, indicate that this reaction will, at hydrogen ion concentrations much below 0.001 M, compete favorably with the solvolysis. We have examined the behavior of I in a zone of such competition, namely, in a sodium acetate–acetic acid buffer, so chosen that the concentrations of salt and acid were approximately equal and twelve times that of I. Under these conditions the rate of release of bromide ion should be approximately of the first order and have an average value close to $k = 3.9 \times 10^{-4}$ min.$^{-1}$ (*e.g.*, $k = k_1 + k_{OAc}$). That this is true of the rate, measured not only in terms of release of bromide ion, but also (spectrophotometrically) in terms of the amount of ketone (III) produced with time, follows from the data of Table VI. Thus, the spectrophotometric data lead to the value[9] $k = 4.08 \times 10^{-4}$ min.$^{-1}$, while from determinations of bromide ion the value[9] 4.12×10^{-4} is obtained.

Furthermore it is to be noted that the ratio of the increment in optical density ($D - D_0$) to that in concentration of bromide ion ($c - c_0$) remains constant with the time and has an average value of 44.8 ± 0.4. Since the value[2] of the molecular extinction coefficient of the ketone (III) is 152, this means that the molar ratio of ketone to total products has a constant value, approximately 0.29. This is to be compared with a predicted value of 0.26 for this ratio obtained by multiplying the ratio k_1/k by the fraction of ketone (0.80) arising from the solvolytic process at this ionic strength.

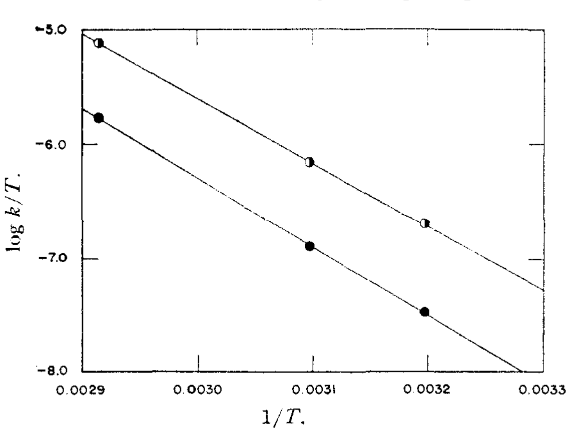


Fig. 1.—Temperature dependence, according to the theory of absolute reaction rates, of rearrangement (◑) and of glycol formation (●) for the solvolysis of I in 70% (aqueous) dioxane; slope = $\Delta H^{\ddagger}/2.303R$.

TABLE VI

REACTION BETWEEN 1,1,2-TRIPHENYL-2-BROMOETHANOL (0.0216 M), ACETIC ACID (0.283 M) AND SODIUM ACETATE (0.286 M) IN 70% (AQUEOUS) DIOXANE AT 40.1°

Time, min.	D^{a}_{340} mμ	Bromide ion (M)	$\Delta D/\Delta[Br]$
0	0.3625	0.00179	
210	.3955	.00359	45.8
450	.4266	.00540	44.4
1080	.4952	.00934	43.9
1585	.5425	.01184	44.8
1890	.5650	.01307	44.9
2455	.6000	.01509	44.6
3960	.6650	.01865	44.9
		Mean	44.8 ± 0.4

[a] In order to compensate for the dilution of the original 10-ml. aliquot to a volume of 25 ml., the values for D given here were obtained by multiplying the observed optical densities by 2.5.

The data of Table VI do not of themselves permit a decision to be reached concerning which of the two possible modes of glycol formation actually operates. But such a decision may be reached by chromatographic analysis of the product of the reaction of I in buffered acetate, since under these conditions the oxide (II) has been found to be stable to hydrolytic attack. If **C** were the precursor of the glycol in ordinary solvolysis, then here it should be expected to lose a proton to the buffered medium and yield, instead, oxide. On the other hand if the glycol is formed by direct interaction with the solvent, this process should be expected to operate quite as well here as in the ordinary solvolysis; hence the glycol should be present in the reaction mixture to the extent of 6.7%. The results of three such chromatographic analyses gave 5.3 ± 1.5% for the glycol content.

Apparently, then, little if any participation by C_β–OH occurs in this system, probably because of steric strain in **C** which would require *cis* juxtaposition of two phenyl groups. The previously described effect of silver and mercuric ions in causing exclusive production of ketone would seem, therefore, traceable to the capacity of these ions to enhance the intramolecular process (rearrangement) more effectively than the intermolecular one (glycol formation).

From the rates of solvolysis in 70% dioxane and the product compositions previously reported[2] it is possible to estimate the relative contribution (k_{Ph}, k_{OH}) of the two processes to the total rate, since it is assumed that at a given temperature

$$k_1 = k_{Ph} + k_{OH};\ k_{Ph}/k_{OH} = \%\text{III}/\%\text{IV}$$

Furthermore, from these data with the aid of the Eyring equation

$$k = (\mathrm{k}T/\mathrm{h})\,e^{-\Delta F^{\ddagger}/RT} = 1.15 \times 10^{12}T\,e^{-\Delta S^{\ddagger}/R}e^{-\Delta H^{\ddagger}/RT}$$

it is possible to obtain graphically, as shown in Fig. 1, values of the free energy, entropy and enthalpy of activation for rearrangement and for glycol formation. Finally, from this equation and the value of k_0 given above, there may be estimated a rough value of the free energy of activation for participa-

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[9] Calculated by the differential method recently described by J. F. Lane and R. L. Feller, THIS JOURNAL, **73**, 4230 (1951).

tion by alkoxide ion. The results of these calculations are given in Table VII.

TABLE VII

THERMODYNAMICS OF ACTIVATION FOR REACTIONS OF I

Product	Temp., °C.	Rate	$\Delta F^{\ddagger}_{298}$, kcal.	$\Delta S^{\ddagger}$, e.u.	$\Delta H^{\ddagger}$, kcal.
Glycol	40	1.03×10^{-5}			
	50	4.20×10^{-5}	28.0	0.8	29.3
	70	5.99×10^{-4}			
Ketone	40	7.47×10^{-5}			
	50	2.29×10^{-4}	26.8	−4.6	25.4
	70	2.52×10^{-3}			
Oxide	25	2.1×10^{6}	11		

The difference in driving force between phenyl and hydroxyl must, therefore, in this system be fairly large (>1.1 kcal). On the other hand, phenyl cannot compete with C_β–O^- when this is present to any significant extent. Indeed, the difference in driving force is so large (16 kcal.) that it is difficult to see how the action of a strong base on I or any remotely similar halohydrin could possibly result in rearrangement. Reports that such is the case[10] are, in our opinion, to be rejected on the ground that the methods of isolation caused rearrangement of epoxide subsequent to its formation.

Experimental

Action of Buffered Acetate on I.—(a) Measurement of Reaction Rate: The data appearing in Table VI were obtained by the same general procedure described above, except that simultaneously with the removal of 20-ml. aliquots for bromide ion analysis there were also removed 10-ml. aliquots for spectrophotometric analysis. These latter samples were immediately diluted with dioxane to 25 ml. in a volumetric flask and analyzed with the Beckman spectrophotometer within a period of 15 minutes.

(b) **Chromatographic Analysis of the Product.**—The product of the reaction was isolated by neutralizing a portion of the original solution with sodium bicarbonate, extracting the resulting mixture with two 30-ml. portions of chloroform and evaporating the combined extracts to dryness under reduced pressure. The weighed residue was dissolved in 40 ml. of 40% isoöctane in benzene, and the solution was allowed to pass through a 12-cm. (25 g.) column of alumina (80–200 mesh, acid-washed at *p*H 3 previously ignited at 170°). Elution of the oxide–ketone fraction was accomplished by the use of 1100 ml. of benzene. The glycol was removed from the column using 100 ml. of acetone as the eluting solvent. The product composition was determined by evaporating both eluents and drying both residues to constant weight. The results of three such determinations were as follows: II–III, 94.7 ± 1.5%; IV, 5.3 ± 1.5%.

Stability of Oxide (II) in Buffered Acetate.—The oxide (II) was subjected to conditions similar to those of the preceding experiment by dissolving 653 mg. (2.4 mmoles) of oxide, 3.920 g. (28.8 mmoles) of sodium acetate trihydrate and 1.657 g. (27.6 mmoles) of glacial acetic acid in sufficient 70% dioxane to give a volume of 100 ml., and allowing the resulting solution to stand at 40° for 11 days (the time required for I to react completely under these conditions). An organic residue weighing 651.4 mg. was then isolated from the reaction mixture by the procedure described in (b) above. The material was then prepared for chromatography by first dissolving the residue in 25 ml. of 40% isooctane in benzene and pouring the solution on an 8 cm. (15 g.) column of alumina (80–200 mesh, acid-washed at *p*H 3 and ignited at 170°). By elution of the oxide–ketone fraction with 250 ml. of benzene there was obtained 641.3 mg. of material (m.p. 75–77°) identified as the oxide (II). This quantity represents a 98.5% recovery of unchanged starting material. No glycol was obtained upon further elution of the column with acetone.

Acknowledgment.—The authors wish to express their appreciation to E. I. du Pont de Nemours and Company for the generous financial support offered during the greater portion of this research.

NEW BRUNSWICK, N. J. RECEIVED JUNE 17, 1949

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[10] M. Tiffeneau and J. Levy, *Bull. soc. chim.*, **33**, 735 (1923); **41**, 416 (1927); **49**, 1661 (1931).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF WASHINGTON]

Fluorination of Pentanes by Cobalt Trifluoride[1]

BY E. J. BARBER, L. L. BURGER AND G. H. CADY[2]

Perfluoro-*n*-pentane, perfluoroisopentane and perfluorocyclopentane have been prepared by the action of hot cobalt trifluoride upon vapors of the parent hydrocarbons. The crude products were separated into their components by careful fractional distillation. Fluorination of neopentane produced numerous substances including perfluoroisopentane. No perfluoroneopentane was found among the products. Each of the crude products of fluorination contained incompletely fluorinated substances and a small proportion of unsaturated fluorocarbon. A complex mechanism which explains the known facts about the reaction of a hydrocarbon with hot cobalt trifluoride has been proposed.

As part of the program of the study of fluorine compounds in these laboratories, it became necessary to prepare a few hundred milliliters each of pure, completely fluorinated hydrocarbons. The present paper tells how the compounds were prepared and discusses the nature of the reactions involved. The properties of the fluorinated compounds are the subjects of other papers.[3]

Of the compounds studied perfluoro-*n*-pentane had been previously prepared by Fowler, *et al.*[4]; and perfluorocyclopentane had been produced by Simons and Block[5] and also by Fowler, *et al.*[4]

Experimental

The method of Fowler and co-workers[4] using hot CoF_3 as the fluorinating agent was chosen for the current work. The net reactions can be represented by the equations $CoF_2 + {}^1/_2F_2 = CoF_3$ and $24CoF_3 + C_5H_{12} = 24CoF_2 + 12HF + C_5F_{12}$.

A 36-mole quantity of cobalt trifluoride was spread into a layer about 12 mm. deep, 20 cm. wide and 2.7 meters long within a reaction vessel made by flattening copper tubing

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[1] Presented at the Meeting of the American Chemical Society, Portland, Oregon, Sept. 1948.

[2] Senior author.

[3] (a) E. J. Barber, THIS JOURNAL, **73**, 4247 (1951); (b) L. L. Burger, *ibid.*, **73**, 4243 (1951); (c) G. H. Rohrback and G. H. Cady, *ibid.*, **71**, 1938 (1949).

[4] R. D. Fowler, W. Burford III, J. Hamilton, Jr., R. Sweet, C. Weber, J. Kasper and I. Litant, *Ind. Eng. Chem.*, **39**, 292 (1947).

[5] J. H. Simons and L. Block, THIS JOURNAL, **61**, 2962 (1939).