## Notes

#### TABLE II

HEAT OF COMBUSTION OF ETHYLENE CARBONATE

Mol. wt. $= 88.062$	
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Sample wt. vac., g. (1)	$\begin{array}{c} \text{Theoretical} \\ \text{CO}_2, \text{ g.} \\ (2) \end{array}$	CO <sub>2</sub> recovered, g. (3)	Δe2, j./ohm (4)	$\Delta R_{\rm c}$ , ohms (5)	q, 28°, j. (6)	21, j. (7)	<sup>q</sup> n, j. (8)	$\begin{array}{c} -\Delta E_{\rm b} \\ 28^{\circ} \\ {\rm j./g. CO_2} \\ (9) \end{array}$
1.60425	2,40522	2.40316	30.6	0.119406	21,513.7	69.0	5.8	8921.1
1.78164	2.67091	2.67106	34.0	.132315	23,840.0	69.0	5.8	8897.3
1.51918	2.27768	2.27775	29.0	.112862	20,334.5	69.0	6.4	8894.3
1.56722	2.34970	2.34799	29.9	.116512	20,992.2	69.0	6.9	8908.2
1.47437	2.21049	2.21037	28.2	. 109697	19,764.2	69.0	5.8	8907.7

Mean 8905.7

Standard dev. of mean  $\pm 4.7$ 

purity. The freezing points listed in the more recent literature, references (4) and (5), although not substantiated, checks more closely the values obtained in this report.

Apparatus and Procedure.—The heat of combustion was determined in a National Bureau of Standards calorimeter, manufactured by the Precision Scientific Company. Resistance measurements were made with Leeds and Northrop type, G-2 Mueller Bridge and a platinum resistance thermometer calibrated by the National Bureau of Standards. All combustions were made in a 340 cc. "Parr" Combustion bomb using purified oxygen. The bath temperature of the calorimeter was maintained at 29.99  $\pm 02^{\circ}$  and calibrated with "Parr" Benzoic acid (calorific value 6318 cal./g.). The sample was dried in a vacuum desiccator at room temperature to constant weight. A moisture analysis by the "Karl Fischer" method showed an insignificant quantity of water.

#### Results

The results of the calibration are listed in Table I. In Table II is listed the results on the heat of combustion of ethylene carbonate. After correcting to  $25^{\circ}$ , constant pressure, and including a modified "Washburn" correction, calculated according to Prosen,<sup>6</sup> a value of  $3179.0 \pm 1.7$  cal./g. is obtained.

Acknowledgments.—The authors wish to acknowledge the assistance of Mr. R. Trask of Picatinny Arsenal, Dover, N. J.

(6) F. D. Rossini, "Experimental Thermochemistry," Editor, Ch. 6, Interscience Publishers, Inc., New York, N. Y., 1956.

# FERROCENE AS A RADICAL "SCAVENGER" IN THE RADIOLYSIS OF CARBON TETRACHLORIDE

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Values of the radical yield,  $G_{\rm R}$ , for the radiolysis of deaerated, liquid carbon tetrachloride, using radiations of comparable linear energy transfer, differ widely. Using diphenylpicrylhydrazyl (DP-PH) as a scavenger, Chapiro<sup>1</sup> obtained 19 ± 1; using the polymerization method, Seitzer and Tobolsky<sup>2</sup> found a value of 10.2; with methyl methacrylate to scavenge the primary radicals and ferric chloride to oxidize the polymethyl methacrylate radicals so formed, the highest value obtained

(1) A. Chapiro, J. Phys. Chem., 63, 801 (1959), and earlier papers cited therein.

(2) W. H. Seitzer and A. V. Tobolsky, J. Am. Chem. Soc., 77, 2687 (1955),

was 8.7<sup>3</sup>; and the radiation-induced exchange of Cl<sup>36</sup>-labelled chlorine with carbon tetrachloride suggests that  $G_{\rm CCl_3} = 3.5 \pm 0.35$  and that  $G_{\rm R}$  is perhaps  $\sim 7.^4$  The solubility of ferrocene (Fn) in this solvent, its small positive oxidation potential and ability to react with free radicals,<sup>5</sup> together with the recent evidence of Brand and Snedden<sup>6</sup> that it can be oxidized by iodine atoms generated photochemically, all point to the probability that ferrocene would efficiently scavenge chlorine atoms produced by irradiation of CCl<sub>4</sub> according to the reaction 1

$$Fn + Cl \longrightarrow Fn^+Cl^-$$
 (1)

where Fn+Cl<sup>-</sup> denotes ferricinium chloride. We here report our observations on this system.

## Experimental

May and Baker carbon tetrachloride was saturated with chlorine and then illuminated for 90 min. with an unscreened medium pressure mercury lamp in a quartz envelope, after which it was washed successively with 5 *M* aqueous NaOH and water, dried over calcium chloride and carefully distilled. Ferrocene was recrystallized once from methanol, dried *in vacuo* and sublimed *in vacuo* at 100° into the empty irradiation cell, the solvent being added subsequently. Co-60  $\gamma$ -rays were used to provide a dose-rate of 3  $\times$  10<sup>19</sup> e.v. l.<sup>-1</sup> sec. in the solution.

Solutions of 5-ml. volume were degassed thoroughly before irradiation. The concentration of ferrocene during an experiment was followed by decanting the sample into a quartz spectrophotometer cell attached to the irradiation cell. Two sintered glass filters of porosities 2 and 3 between the irradiation cell and the spectrophotometric cell prevented the precipitate (Fn +Cl<sup>-</sup>; see Discussion) which was formed from interfering with the spectrophotometric measurements. The molar decadic extinction coefficients, determined from samples of freshly sublimed ferrocene weighed in air, were:  $\epsilon_{max} = \epsilon_{400} = 785$ ;  $\epsilon_{250} = 310$ ;  $\epsilon_{360} = 185$ ;  $\epsilon_{min} = \epsilon_{390} = 67$ ;  $\epsilon_{max} = \epsilon_{400} = 105$ . These values agree as nearly as can be determined with those given in curve (e) of Fig. 1 of reference 6.

### **Results and Discussion**

The variation of [Fn] with dose was measured for solutions containing five different initial concentrations within the range 1.2 to 8.3 mM. In four of these the change in optical density was measured at three different wave lengths and in the fifth solution at two. The graphs of optical density with dose were linear down to a concentration of ~0.5 mM and correspond to  $G(-Fn) = 2.34 \pm 0.07$ .

(3) N. Colebourne, E. Collinson and F. S. Dainton, unpublished work.

(4) J. W. Schulte, J. Am. Chem. Soc., 79, 4643 (1957).

(5) P. L. Pauson, Quart. Revs., 9, 391 (1955).

(6) J. C. D. Brand and W. Snedden, Trane, Foraday Soc., 53, 894 (1957).

There was evidence for a small back reaction in that the initial slope at 307 m $\mu$  of a solution of initial concentration 1.2 mM was 0.052 whereas the slope for a solution in which the concentration had been reduced by irradiation from an initial value of 8.3 to 1.2 mM was 0.037. The possibility that the irradiation products of pure carbon tetrachloride in some way affect the ferrocene or other products was excluded by direct experiment.

To test the stoichiometry of the reaction, dry methanol was added under vacuum to the residue after the solvent had been pumped off an irradiated solution. The resulting solution was blue. having an absorption peak at  $620 \text{ m}\mu$ . If this peak were due entirely to the ferricinium ion for which  $\epsilon_{620} = 362$  in methanol,<sup>6</sup> then the concentra-tion of Fn<sup>+</sup>Cl<sup>-</sup> present was within 5% of that of the ferrocene destroyed.

When a sufficiently large dose had been given completely to destroy the ferrocene, a small new absorption band  $(\lambda_{max} 320 \text{ m}\mu)$  was observed. This was not due to chlorine which in carbon tetrachloride solution has a spectrum with  $\lambda_{max}$  332 m $\mu$ . Possibly a substituted ferrocene is responsible for this band. If so the yield is small.

If reaction 1 were the only origin of  $Fn^+Cl^-$  then we could conclude  $G_{Cl} = 2.34$ . However it is possible that ferrocene may be oxidized by CCl<sub>3</sub>+ (an abundant ion in the mass spectrum of  $CCl_4$ ) and  $CCl_3$  (almost certainly the precursor of the  $C_2$ - $Cl_6$  found when pure  $CCl_4$  is irradiated). It is also possible that a fraction of such reactive radicals as chlorine atoms may abstract a hydrogen atom, the resultant ferrocene radical being the immediate precursor of the substituted ferrocene thought to be responsible for the spectrum with  $\lambda_{max}$  at 332 m $\mu$ . An attempt to measure G(HCl) for a ferrocene solution was unsuccessful due to obscuration of the end-point by Fn and Fn+Cl-.

We conclude that although solutions of ferrocene in carbon tetrachloride respond to irradiation in a typical "indirect action" manner the value of  $\tilde{G}(-Fn) = G(Fn+Cl^{-}) = 2.34$  is merely a minimum value for  $G_{\rm R}$ .

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## THE REACTION OF TOLUENE-2,4-DIISOCYANATE WITH *n*-BUTYL ALCOHOL

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Although numerous studies of isocyanate concentration vs. time for the reaction of toluene- $2,4\text{-diisocyanate}\ (\text{TDI})$  with a primary alcohol have appeared in the literature, 1-5 no analysis of the data

(1) I. C. Kogon, J. Org. Chem., 24, 438 (1959).

(2) M. E. Bailey, et al., Ind. Eng. Chem., 43, 794 (1956).

(3) M. Morton and M. A. Deisz, Abstracts of Papers, Div. of Paints and Plastics, A.C.S. Meeting, September, 1956.
(4) J. J. Tazuma and H. K. Latourette, ref. 3.

(5) J. Burkus and C. F. Eckert, J. Am. Chem. Soc.. 80, 5948 (1958).

has ever been reported giving the concentrations of TDI, intermediates, and final product throughout the course of the reaction. Such data, applied to recently derived equations,<sup>6</sup> would permit more detailed characterization than has heretofore been possible of an important class of condensation polymers, polyurethans derived from TDI. Consequently, the following experiment and analysis were undertaken.

TDI was treated with n-butyl alcohol-xylene solution at 80°. The concentration of -NCO as a function of time was determined by transferring periodically withdrawn reaction samples to excess *n*-butylamine solution and back titrating with HCl. A representative curve is shown in Fig. 1. Values of -NCO, as read from the smoothed out curve of Fig. 1 are compiled in Table I, col. 2.

#### TABLE I

COMPARISON OF EXPERIMENTAL CONCENTRATIONS OF ISO-CYANATE WITH CALCULATED VALUES

Time, hr.	Exp	tl.	Calc	d. 1	Caled. 2
0	0.2	50	0.25	000	0.25000
0.100	.2	24	.22	235	.22244
.200	.2	05	.20	208	.20217
.300	.1	87	.18	657	.18664
.400	.1	73	.17	433	.17438
. 500	.162			443	.16444
.750	.1	46	.14	635	.14630
1.000	.1	34	.13	409	.13400
1.250	.126		.12520		.12511
1.500	.118		.11843		.11834
1.750	.113		.11307		.11300
2.000	.109		.10869		.10865
2.500	.102		.10189		.10190
3.000	.097		.09673		.09680
4.000	.090		.08914		.08925
5.000	.084		.08352		.08358
6.000	.0	78	.07900		.07894
Constants (l./eqhr.)	$k_1$	$k_2$	k:	k.	Std. deviation meq./ml.
Calcd. 1	8.54	4.00	1.92	0.53	0.00118
Calcd. 2	9.21	6.00	1.20	0.63	0.00115

Assuming that reaction of each -NCO group in eq. 1 with a primary alcohol obeys second-order kinetics,<sup>7</sup> one obtains the following set of independ-



(6) A. Di Giacomo, J. Poly. Sci., in press.

(7) R. G. Arnold, et al., Chem. Revs., 57, 47 (1957).