under its surface. The photolysis cell had a quartz window. The quantum yields given in Table IV were calculated from the instantaneous rate of the azide photolysis at 20% completion. Because of adventitious oxygen, quantum yields calculated from initial rates are of little quantitative significance.

Table IV. Quantum Yield (Φ) at 20% Completion in Direct Photolysis of Methanesulfonyl Azide in Isopropyl Alcohol

Intensity × 10^6, einstein $l.^{-1}$ sec^{-1}	$[CH_3SO_2N_3]_0$, *M*	Φ, moles $einstein^{-1}$
1.05	0.083	111
1.08	0.088	124
1.21	0.082	126
0.85	0.092	153

D. **Thermolysis of *p*-Bromobenzenesulfonyl Azide in Aqueous Isopropyl Alcohol.** The results obtained with *p*-bromobenzenesulfonyl azide were similar to those with other azides. The azide (0.715 g, 0.0028 mol) in isopropyl alcohol (72 ml) and water (8 ml) in a foil-wrapped flask was degassed by passage of nitrogen under its surface and refluxed (78°) with stirring until infrared spectra of aliquot residues showed no unchanged azide (5 hr). Evaporation left *p*-bromobenzenesulfonamide, 0.615 g (98%, corrected for aliquot removal), mp 165.5–166.5°. Repeated recrystallizations from 1:1 95% ethanol–water gave constant mp 166–167.5°, not depressed by mixture with authentic *p*-bromobenzenesulfonamide.

E. **Ferrous Chloride Induced Reaction of α-Toluenesulfonyl Azide with Isopropyl Alcohol.** To preclude interference from peroxides, freshly purified isopropyl alcohol was distilled (in a system gently swept with nitrogen) from anhydrous stannous chloride into a fraction cutter, from which 60 ml of the alcohol was measured into a nitrogen-purged flask separated from the atmosphere by a mercury trap. The flask was equipped with a reflux condenser and a dropping funnel containing a nitrogen-washed aqueous solution of 0.33 *M* ferrous chloride[39] in 2.4 *M* hydrochloric acid. A Teflon bucket containing α-toluenesulfonyl azide (0.736 g, 0.00373 mol) was suspended in the condenser. The stirred alcohol was heated to 75°, and the azide was dropped into the liquid; it dissolved with no sign of reaction. Addition of ferrous chloride solution (0.75 ml, 5×10^{-4} mol) caused vigorous nitrogen evolution lasting *ca.* 1 min. The cooled reaction mixture was diluted with water to 100 ml, and a portion (40 ml) was combined with 2,4-dinitrophenylhydrazine solution prepared from 1.2 g (0.006 mol) of the reagent. The mixture stood overnight and was chilled, and acetone–DNP (0.426 g; 98% corrected) was collected. Recrystallization from 95% ethanol gave constant mp 125–126°, not depressed by mixture with an authentic sample.

Evaporation of the remaining portion of the reaction mixture left a solid which was triturated and centrifuged with warm aqueous 5% NaOH (4 ml, then five 2-ml portions) to precipitate the iron. The combined supernatants, after being acidified with concentrated hydrochloric acid and chilled, gave α-toluenesulfonamide, which was washed with a little ice water, 0.253 g (78%, corrected), mp 103.5–104°, unchanged by recrystallization from 2:3 Skellysolve–ethyl acetate, and not depressed by mixture with an authentic sample.

Acknowledgment. We thank Drs. J. B. DiGiorgio, D. O. Cowan, and H. H. Seliger for many helpful discussions, and Mr. J. A. Walter for help with apparatus design and construction.

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The Kinetics of the Photochemically Initiated Condensation Reaction between Tetrachloroethylene and *n*-Pentane[1a]

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Abstract: The kinetics of the photochemically initiated radical chain condensation reaction between tetrachloroethylene and *n*-pentane, resulting in the formation of pentyltrichloroethylene and HCl have been studied at 25°. The absolute rate constant for the rate-determining step, the addition of pentyl radicals to tetrachloroethylene, is estimated as 6.6×10^2 M^{-1} sec^{-1}, by combining rate constant ratios from kinetics with alkyl radical combination data.

The addition of alkyl radicals to substituted olefins is known to be affected both sterically and by polar effects. Szwarc, *et al.*,[1b] have found that in the case of addition of methyl radicals to ethylene, the substitution of all hydrogen by fluorine atoms resulted in a tenfold increase in the rate of addition. This enhanced rate of addition was attributed by the authors to the fact that electron-withdrawing substituents weaken the repulsion between the negative cloud of π electrons of the olefin and of the p electrons of the attacking radical thus lowering the activation energy of the addition reaction. However, in the case of methyl radical addition to tetrachloroethylene the rate of addition was found to only $^1/_{90}$ of that observed in the case of ethylene. The pronounced lack of reactivity of tetrachloroethylene toward methyl radical addition was attributed to steric hindrance, the bulky chlorine obstructing the approach of the alkyl radical.

The facts that no polymerization of tetrachloroethylene was observed under free radical initiation[2] and that very limited copolymerization with other monomers was obtained[3] seem to support Szwarc's finding that the process of addition of alkyl radical to tetrachloroethylene proceeds very sluggishly.

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[1] (a) This paper is based upon a dissertation to be submitted by A. Horowitz in partial fulfillment of the requirement for the Ph.D. degree in chemistry, at the Hebrew University, Jerusalem; (b) R. P. Buckley and M. Szwarc, *J. Am. Chem. Soc.*, 78, 5696 (1956).

[2] K. W. Doak, *ibid.*, 70, 1525 (1948).

[3] A. Turner and S. Grenberg, *J. Polymer Sci.*, 3, 237 (1948).

These facts seem to be hard to reconcile with the substantial evidence[4] that free-radical-type condensation reaction occurs quite readily between tetrachloroethylene and alcohols, esters, aldehydes, and paraffins. In a previous communication[5] evidence was reported that upon γ radiolysis of solutions of tetrachloroethylene in *n*-pentane, pentyltrichloroethylene is formed following an interaction between pentyl radicals and tetrachloroethylene. Since, during radiolysis, charged species are generated and part of the products formed may result from ion–molecule reactions, it was thought worthwhile to initiate the formation of alkyl radicals by photochemical means and reinvestigate the mechanism of addition of pentyl radicals to tetrachloroethylene, with a view to determine the rate constant for the addition reaction.

Experimental Section

Materials. Pentane (Phillips Research Grade) was shaken overnight with $^1/_{10}$ its volume of concentrated sulfuric acid. The organic layer was then washed away with water and dried over anhydrous calcium carbonate. Tetrachloroethylene (Matheson Spectrograde) was distilled under nitrogen and stored over sodium carbonate.

Procedures. Standard *n*-pentane solutions were prepared and 2-ml aliquots were placed in Pyrex reaction vessels consisting of a 20-mm diameter tube sealed at one end and fitted with a break seal and standard taper joints at the other. The vessels were then attached to the vacuum line and the solution thoroughly deaerated by the freeze–thaw method until a vacuum of at least 10^{-5} mm was obtained. The solutions were then irradiated. The ultraviolet source was a high-pressure mercury lamp (Quartz-Lampen Geseltschaft, Hanau Type PL 321). The source was mounted vertically on an optical bench, so that radiation intensity incident on the sample could be varied by altering the lamp–reaction vessel distance. The samples were fan cooled. The liquid products were analyzed by gas chromatography (F & M Model 810) using a column of 20% Ucon on Chromosorb S. Pentyltrichloroethylene was identified by combustion analysis and mass spectrometric analysis.

Anal. Calcd for $C_7Cl_3H_{11}$: C, 41.7; Cl, 52.7; H, 5.5. Found: C, 42.8; Cl, 50.7; H, 6.3.

Trichloroethylene was identified by gas chromatographic retention time comparison with authentic samples and mass spectrometry analysis. In order to determine the yield of hydrogen chloride the irradiated samples were frozen at liquid air temperature and opened under a layer of 5 ml of H_2O. The aqueous layer was separated and its HCl content determined coulometrically using the Aminco-Cotlove chloride titrator.

Results and Discussion

The mode of photodecomposition of haloethylenes has attracted very little attention. In the case of *cis*-1,2-dichloroethylene it has been suggested[6] that both radical and molecular modes of decomposition are operative. We assume that in view of the low energy involved in the irradiation (the irradiated cell being made of Pyrex glass) the primary step in the photochemical process is

$$C_2Cl_4 \xrightarrow[h\nu]{K_0I} C_2Cl_3 + Cl \qquad (1)$$

This assumption is supported by the fact that no dichloroacetylene could be detected among the products of decomposition.

The products of the decomposition of tetrachloroethylene would be expected to react very efficiently with the solvent, yielding trichloroethylene and hydrogen chloride. The fact that no hexachlorobutadiene was found among the products supports this assumption. Other chlorine-bearing products found in significant yield were pentyltrichloroethylene and pentyl chloride. The chlorine balance based on the products was satisfactory (see Table I). Thus no chlorine-combining products of any importance are produced besides those determined. The major nonchlorinated product determined was decane.

Table I. Rate of Formation of Products[a] in the Photolysis of Solutions of Tetrachloroethylene in *n*-Pentane

C_2Cl_4 concn, m*M*	$C_{10}H_{22}$	$C_5H_{11}Cl$	C_2Cl_3H	C_7Cl_3-H_{11}	HCl	I/II[b]
30.5	12.5	5.35	33.4	21	50.5	1.03
61	18.7	7.25	51.5	48	96.5	1.02
122	19.1	9.25	59.5	89	165.0	1.05
180	21.1	13.2	62.5	141	195.0	0.99
245	23	18.5	69.5	195	240.0	1.02
490	19.4	23.9	74.5	328	439.0	1.14
980	14.1	24.1	87.5	593	685.0	1.04

[a] In mole $l.^{-1}$ $sec^{-1} \times 10^8$. [b] $I = ([C_5H_{11}Cl] + [HCl])$; $II = ([C_2Cl_3H] + [C_7Cl_3H_{11}])$.

The yields of all the products determined were found to increase with growing concentration of the solute, the products most affected by the increase in solute concentration being pentyltrichloroethylene and hydrogen chloride. The sum of the yields of hydrogen chloride and chloropentane equalled the sum of the yields of trichloroethylene and pentyltrichloroethylene. With the increase in tetrachloroethylene concentration the yield of pentyltrichloroethylene and hydrogen chloride became considerably higher than the yield of trichloroethylene. The yield of pentyltrichloroethylene was found to depend linearly on the square foot of the incident radiation intensity both at 0.18 and 0.5 *M* concentration of solute (see Figure 1). This finding precludes the possibility that pentyltrichloroethylene is formed mainly by bimolecular radical combination reaction, in which case one would expect the yield of pentyltrichloroethylene to depend linearly on the first power of the light intensity. The fact that the ratio of the slopes of the two lines shown in Figure 1 is equal to the ratio of the solute concentrations indicates that pentyltrichloroethylene formation is first order in respect to C_2Cl_4 concentration. On the basis of the foregoing the scheme shown in eq 2–6a is suggested for the formation of the products.

$$Cl + C_5H_{12} \longrightarrow HCl + C_5H_{11} \qquad (2)$$

$$C_2Cl_3 + C_5H_{12} \longrightarrow C_2Cl_3H + C_5H_{11} \qquad (3)$$

$$C_5H_{11} + C_2Cl_4 \longrightarrow C_7H_{11}Cl_4 \qquad (4)$$

$$C_7H_{11}Cl_4 \longrightarrow C_7H_{11}Cl_3 + Cl \qquad (5)$$

$$C_5H_{11} + C_5H_{11} \longrightarrow \left[\begin{array}{ll} C_{10}H_{22} & \qquad (6) \\ C_5H_{10} + C_5H_{12} & \qquad (6a) \end{array}\right.$$

Inherent in the eq 2–6a is the assumption that the radical $C_7H_{11}Cl_4$ is short lived and decomposes by splitting of a chlorine atom before it can react either with the solvent or with other radicals. An alternative

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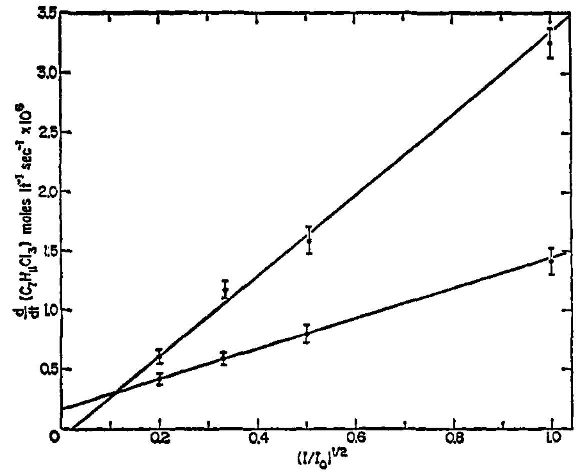

Figure 1. The rate of formation of $C_7H_{11}Cl_3$ as a function of square root of light intensity at 0.18 (lower line) and 0.5 *M* concentrations of C_2Cl_4.

scheme which could account for the products would entail abstraction of hydrogen atom from the solvent by the $C_7H_{11}Cl_4$ radical, followed by the breakdown of the product into pentyltrichloroethylene and HCl.

$$C_7H_{11}Cl_4 + C_5H_{12} \longrightarrow C_7H_{12}Cl_4 + C_5H_{11} \quad (7)$$

$$C_7H_{12}Cl_4 \longrightarrow C_7H_{11}Cl_3 + HCl \quad (8)$$

However, hydrogen chloride elimination from monochloroalkanes entails relatively high activation energy of approximately 50 kcal/mol,[7] while the dehydrohalogenation reaction of polyhalogenated alkanes requires even higher activation energies.[8] Thus on thermodynamic grounds one would hardly expect reaction 8 to occur at room temperature.

The fact that chloropentane is found among the products of photolysis might suggest the occurrence of yet an additional termination step

$$C_7H_{11}Cl_4 + C_5H_{11} \longrightarrow C_7H_{11}Cl_3 + C_5H_{11}Cl \quad (9)$$

We observe, however, that within a concentration range of 6 × 10^{-2} to 4.9 × 10^{-1} *M* tetrachloroethylene, the steady state of pentyl radicals as measured by the yield of decane remains practically constant (see Table I). If reaction 9 would constitute the only mechanism by which chloropentane is formed, then the ratio of the yields of $C_7H_{11}Cl_3$ to $C_5H_{11}Cl$ should remain almost constant. Actually, we find that in the above concentration range of solutes $C_7H_{11}Cl_3$ increases faster than $C_5H_{11}Cl$ by a factor of 2.1 suggesting that chloropentane is formed by a side reaction which does not affect the kinetic scheme suggested. However, it is conceivable that in cases where the addition of other alkyl radicals to chloroolefins forms intermediate radicals of longer lifetime than that of $C_7H_{11}Cl_4$, one would have to consider reaction 9 as a chain termination step.

Kinetics of the Formation of Pentyltrichloroethylene

According to the mechanism proposed the formation of pentyl trichloroethylene and decane is given by

$$d[C_7H_{11}Cl_3]/dt = k_4[C_5H_{11}][C_2Cl_4] \quad (10)$$

$$d[C_{10}H_{22}]/dt = k_6[C_5H_{11}]^2 \quad (11)$$

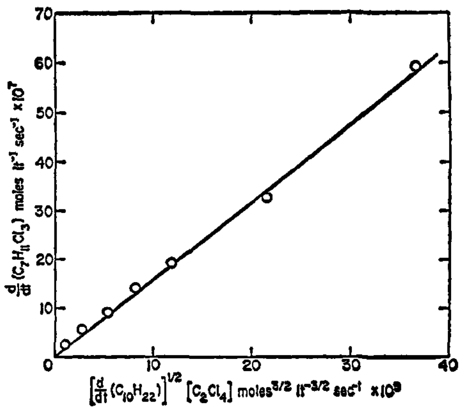

Figure 2. The rate of formation of $C_7H_{11}Cl_3$ as a function of $(d[C_{10}H_{22}]/dt)^{1/2}[C_2Cl_4]$, expression 12.

Combining expressions 10 and 11 we obtain

$$\frac{d[C_7H_{11}Cl_3]}{dt} = \frac{k_4}{k_6^{1/2}}\left(\frac{d[C_{10}H_{22}]}{dt}\right)^{1/2}[C_2Cl_4] \quad (12)$$

The fact that expression 12 is obeyed in the concentration range 3 × 10^{-2} to 1 *M* of solute (see Figure 2) seems to confirm the chain mechanism proposed. From the slope of the straight line of Figure 2 we obtain a value of 1.6 × 10^{-2} for the ratio $k_4/k_6^{1/2}$.

The only available data for alkyl radical combination in the liquid phase are those of ethyl radicals. Fessenden and Schuler[9] have found that the rate constant for ethyl radical interaction in the liquid phase at room temperature equals 3.39 × 10^9 M^{-1} sec^{-1}.

The rate constant for pentyl radical combination can be well expected to be very close to that of ethyl radicals. However, the rate constant determined by Fessenden and Schuler referred mainly to the combination reaction. In the case of the pentyl radical one has also to consider the disproportionation reaction (reaction 6a).

In the mercury-photosensitized decomposition of liquid *n*-hexane the ratio of $K_{\text{disproportionation}}/K_{\text{combination}}$ of the hexyl radical at room temperature has been found to equal unity.[10] Although a somewhat different distribution of primary and secondary radicals may be expected in the present case, it may be assumed that no significant error will be introduced if we consider that the ratio of k_6/k_{6a} in *n*-pentane as 1. Substituting the value of 1.7 × 10^9 for k_6 we obtain the value of 6.6 × 10^2 M^{-1} sec^{-1} for k_4. This value is quite close to the rate constant of addition of methyl radicals to ethylene in the gas phase, namely 1 × 10^3 M^{-1} sec^{-1}.[11]

Smid and Szwarc[12] claim that no difference is observed in the rate constants for addition of methyl and ethyl radical to olefins. Similarly one might expect that no pronounced difference should exist between the affinity of methyl or pentyl radicals toward ethylene. Our results would thus imply that addition of non-

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branched alkyl radical to tetrachloroethylene in the liquid phase proceeds almost as efficiently as the addition of methyl radicals to ethylene in the gas phase.

The fact that Szwarc[1b] has found that the addition of methyl radicals to tetrachloroethylene does not proceed efficiently might be due to the unsuitability of his measuring technique in a system containing tetrachloroethylene. The method developed by Szwarc uses the thermal decomposition of acetyl peroxide as a source of methyl radicals. The methyl radicals abstract hydrogen from the solvent (isooctane), forming methane. In the presence of solutes consuming methyl radicals, a net decrease in the amount of methane formed is observed. The difference in methane formed in the presence and absence of a solute constitutes a measure of its affinity toward methyl radicals. In the particular case of tetrachloroethylene, a chain reaction between the solvent radicals and tetrachloroethylene could ensue, similar to the reaction observed in this work. The formation of HCl in the system might induce decomposition of the acetyl peroxide, resulting in an increased rate of methyl radical generation. The enhanced rate of methyl radicals formation could thus mask their disappearance by interaction with the solute. Under such circumstances, a fortuitously low value for methyl radical addition to tetrachloroethylene could be obtained.

Our results would imply, assuming comparable rates for the addition of radicals to olefins in the liquid and gaseous phase, that the steric hindrance caused by the presence of the bulky chlorine atoms in tetrachloroethylene is almost completely offset by the inductive effect of the halogen substituents.

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Kinetics of the Addition of Methylmagnesium Bromide to 4-Methylmercaptoacetophenone in Diethyl Ether[1]

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Contribution from the Department of Chemistry, University of Illinois, Urbana, Illinois 61801. Received January 5, 1968

Abstract: The ultraviolet spectrum of reacting solutions of 4-methylmercaptoacetophenone in ether solutions of methylmagnesium bromide at 25.0° has been found to exhibit an absorbance, λ_{max} 336 mμ (ϵ 1.5 $\times$ 10^4), corresponding to complex formation with an apparent equilibrium constant of 15 l./mol. The pseudo-first-order rate constant for the addition of methylmagnesium bromide to the carbonyl group increases from 0.3 to 1.3 sec^{-1} with an increase in the Grignard concentration from 0.05 to 0.6 *M*. Reaction schemes involving conversion of the complex to product which provide a descriptive summary of these data are outlined. A twofold decrease in pseudo-first-order rate constant with an increase in ketone concentration by a factor of *ca.* 10, esr signals, and an absorption spectrum, λ_{max} 334 and 560 mμ, observed during the reaction of methylmagnesium bromide with benzophenone, as well as the formation of benzopinacol in 14% yield from 9.6 $\times$ 10^{-3} *M* ketone and 2 *M* Grignard, suggest the presence of a ketyl-like side reaction in this system.

Recent studies[3] have suggested that formation of a complex between Grignard reagents and ketones is fast[4–6] on the time scale of conversion of reactants to products. However, the nature of the reactive species in the Grignard reagent and details of the product-forming steps require further clarification. The early suggestion of Meisenheimer and Casper[7] that a complex between the Grignard reagent and ketone is converted to product by a unimolecular process has received substantial support.[4–6,8–10] Other data[11–13] have been interpreted as inidicating that in the product-forming step, the complex reacts with a second molecule[14] of organomagnesium reagent.

In a previous spectroscopic and kinetic study of the reaction of methylmagnesium bromide with 2,4-dimethyl-4′-methylmercaptobenzophenone in diethyl ether,[4] below *ca.* 0.3 *M* methylmagnesium bromide, data were found to be quantitatively consistent with unimolecular conversion of complex to product, while above *ca.* 0.3 *M* the reaction was found to be faster

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(2) Sinclair Oil Predoctoral Fellow.

(3) For reviews see: (a) B. J. Wakefield, *Organometal. Chem. Rev.*, **1**, 131 (1966); (b) W. Tochtermann, *Angew. Chem.*, **5**, 351 (1966); (c) R. E. Dessy and W. Kitching, *Advan. Organometal. Chem.*, **4**, 280 (1966); (d) E. C. Ashby, *Quart. Rev.* (London), **2**, 259 (1967).

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