TABLE III

SUMMARY OF RATE RUNS AT THREE TEMPERATURES, IN ACETIC ACID, FOR THE REACTION OF 2,4-DINITROBENZENESULFENYL CHLORIDE AND *trans*-STILBENE

Run	Stilbene, mole/l.	ArSCl, mole/l.	$k \times 10^{-3}$, (mole/l.)$^{-1}$ sec.$^{-1}$	Mean value of $k \times 10^{-3}$	T, °C.
1	0.05152	0.05251	1.83		
2	.05755	.05251	1.86	1.85 ± 0.03	45.0 ± 0.1
3	.05148	.03706	3.07		
4	.06452	.03706	2.96	3.00 ± .03	55.0 ± .1
5	.06681	.03706	2.98		
6	.03064	.03348	4.09		
7	.02964	.03348	4.16	4.08 ± .06	63.0 ± .1
8	.03034	.03348	3.99		

TABLE IV

DATA FOR A TYPICAL RUN IN ACETIC ACID[a,b]

Time, min.	$S_2O_3^=$ 0.0328 N, ml.	$(a - x)$ ArSCl	$(b - x)$ Stilbene	$\log \frac{b(a-x)}{a(b-x)}$	$k \times 10^{-3}$, (mole l.)$^{-1}$ sec.$^{-1}$
0	16.01	0.05251	0.05152	....	..
243	13.65	.04470	.04371	0.0138	2.17
566	11.62	.03820	.03721	.0305	2.09
1482	8.83	.02897	.02798	.0675	1.75[c]
1951	7.47	.02450	.02351	.0957	1.88
3120	5.80	.01904	.01805	.1484	1.82
4610	4.40	.01442	.01343	.2254	1.86

[a] Run 1 of Table III. [b] Sample volume was 10 ml. [c] Based on last four points, the mean value of $k \times 10^3 = 1.83$.

Data for runs of *trans*-stilbene in acetic acid are summarized in Table III, and details for a typical run are listed in Table IV. From the data of individual runs, excellent second-order plots resulted. All the runs were followed to at least 70% completion. In determining the mean values of the constants in Tables I and III, points below 10–15% completion of reaction were excluded. The concentration of sulfenyl chloride was calculated from the corrected volume of thiosulfate solution used.

The initial concentration of stilbene was calculated from the known weight of olefin introduced into the reaction mixture and that of I was determined by titrating aliquots of the freshly prepared solution of I.[12]

The concentration of olefin in the solution was calculated from the measured concentration of the sulfenyl chloride and the difference in initial concentrations of the two reactants. The specific reaction rate constants were calculated from the familiar second-order expression

$$k = \frac{2.303}{x(a - b)} \log \frac{b(a - x)}{a(b - x)}$$

The plot of log k *vs.* $1/T$ for the runs in acetic acid gives an excellent linear relation; the slope of this line gives 9.4 kcal./mole for the activation energy of the reaction of *trans*-stilbene with I from which is calculated the values of $\Delta F^{\ddagger}$ and $\Delta S^{\ddagger}$, which are 22.0 kcal./mole and −41.55 cal./degree mole, respectively. The slope of the line for the reaction of *cis*-stilbene with I gives 13.8 for the activation energy from which the calculated values of $\Delta F^{\ddagger}$ and $\Delta S^{\ddagger}$ are 23.0 and −28.78 cal./degree mole, respectively. The reaction of *trans*-stilbene with I showed a positive salt effect with added lithium chloride.

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[12] N. Kharasch and M. Wald, *Anal. Chem.*, **27**, 996 (1955).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF SOUTH CAROLINA, COLUMBIA, S. C.]

The Reactivity of the 1-Hexyl Radical in Abstracting Hydrogen and Halogen Atoms[1,2]

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This paper reports the first quantitative investigation in solution of atom abstraction reactions of a primary alkyl radical (other than the exceptional methyl radical). Decomposition of *n*-heptanoyl peroxide gives products derived from 1-hexyl free radicals. By using solvent mixtures containing both a hydrogen-donor and a halogen-donor (usually carbon tetrachloride) and by measuring the relative yields of hexane and 1-chlorohexane it is possible to take the production of 1-chlorohexane as a pilot reaction against which the rates of a series of hydrogen abstraction reactions can be measured. The relative rates for some thirty abstraction reactions are reported in Tables II and III. Absolute rate constants are not available at present. Also for the first time the validity of this procedure has been reliably established. The requirements and the assumptions are considered critically. In addition detailed product studies in five solvent mixtures and with a wide variation in compostion show that the mechanism of the decomposition of *n*-heptanoyl peroxide is closely similar to that of the previously studied δ-phenylvaleryl peroxide. About 50% of the radicals from both peroxides are involved in geminate reactions. Interestingly the ratio of geminate disproportion to combination for 1-hexyl radicals is 0.15, a value similar to the ratios for ethyl and 1-propyl free radicals in the gas phase. The main features of the decomposition of peroxides of the structure $(RCH_2CH_2COO)_2$ can now be considered to be established.

Introduction.—Quantitative reactivity measurements have been reported for a number of free radical reactions involving atom abstraction (also called chain transfer or metathesis). Methyl radicals from the photolysis of acetone or of dimethylmercury or from thermal decomposition of di-*t*-butyl peroxide have been extensively studied in the gas phase.[4] One study has been made in solution.[5] Extensive data are available for a few

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[1] Diacyl Peroxide Reactions. VI; previous paper, D. F. DeTar and R. C. Lamb, THIS JOURNAL, **81**, 122 (1959).

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[4] Reviewed by (a) A. F. Trotman-Dickenson, *Quart. Revs.*, **7**, 198 (1953); (b) A. F. Trotman-Dickenson, "Gas Kinetics," Butterworths, London, 1955.

[5] F. G. Edwards and F. R. Mayo, THIS JOURNAL, **72**, 1265 (1950).

Table I

Products of the Thermal Decomposition of *n*-Heptanoyl Peroxide in Solvent Mixtures[a]

$\frac{(CCl_4)}{(SH)}$	Hexane	1-Chlorohexane	Dodecane	1,1,1,3-Tetrachloroheptane	*n*-Hexyl heptanoate	C_2Cl_6			Other products
				Benzene and CCl_4					
4.10	2.6	95	22	8.2	15	45			b,c,d,e
2.63	2.5	94	18	7.7	13	39			
1.98	2.8	92	22	7.4	14	42			
0.95	2.9	93	20	8.0	14	40			
.59	2.8	91	18	8.7	12	32			
.32	3.1	93	16	8.9	11	29			
.25	2.6	90	20	6.9	10	29			
Av.	2.8	93	19	8.0	12	..			
				Toluene and CCl_4					
3.76	2.5	98	25	9.1	10	6			d,f
3.01	2.6	98	25	8.2	10	6			
2.09	2.9	98	30	8.9	13	4			
1.05	3.1	101	29	8.2	14	3			
0.52	3.8	91	30	9.6	11	2			
.33	4.3	86	24	8.7	14	2			
.24	4.6	78	27	9.0	11	..			
Av.	2.8[g]	99[g]	27[h]	8.8	11.5	..			
				Acetone and CCl_4					
							Chloroacetone		
3.85	3.7	103				52	12		c,d,l,m
3.08	2.7	102				45	11		
1.97	3.8	102				43	13		
0.98	3.5	97				41	11		
.49	4.0	98				34	14		
.34	4.7	101				36	14		
.25	5.3	102				33	13		
.065[i]	15.7	82	14	4.9	8	26	..		
.050[j]	19.2	80	14	4.2	8	25	..		
.033[i]	26.7	76	13	3.5	8	21	..		
Av.	..	101[k]	14	4.2	8	..	11		
				Cyclohexane and CCl_4					
							$CHCl_3$	$C_6H_{11}Cl$*	
4.33	4.6	91	21	9.7	14	51	520	490	c,d,o
2.77	5.7	102	22	9.2	14	54	750	720	
1.69	6.2	92	23	9.5	14	56	820	810	
1.00	8.3	84	20	8.8	12	51	930	1140	
0.54	12.2	85	20	9.2	12	44	1150	1300	
.32	13.7	79	19	8.7	11	49	1400	1400	
.27	12.1	75	17	9.1	10	32	1500	1400	
Av.	..	..	20	9.2	13	..	..	..	
				$CHCl_3$ and CCl_4					
CCl_4[p]	3.8	88	18	7.3	12	43			c,s
CCl_4	..	93							
CCl_4	1.8	88	23	8.4	16	44			
2.87[q]	14	80							
1.74[q]	20	76							
1.00[q]	28	57							
0.46	39	49							
.23	43	47							
.11	77	26	21	6.3	12	43			
.058[r]	70	14							
$CHCl_3$[q]	90	5							
Av.			21	7.3	13				

[a] Unless otherwise noted the mole fraction of peroxide was 0.010–0.011 (*ca.* 0.1 *M*). The reaction was carried out at 74° for 48 hours; reaction mixtures were outgassed to remove oxygen. Product yields are given as mole per cent. (*i.e.*, 100 × moles of product per mole of peroxide). [b] Chlorobenzene was absent (less than 3 mole per cent.). [c] Less than 4% of 2-chlorohexane was present. [d] Less than 3% of 1,1,1-trichloroheptane was present. [e] Approximate yield of heptanoic acid was 16 mole per cent.; 92% of hexyl groups accounted for. In carbon tetrachloride the carbon dioxide yield was estimated as 162 mole per cent. [f] Approximate yield of heptanoic acid was 1%; 94% of hexyl groups accounted for. [g] Average of first four runs. [h] This appears to be high, and it is possible that some unidentified product has the same retention time. [i] Peroxide mole fraction 0.0053. [j] 0.004. [k] Av. of first 7 runs. [l] Acetonylacetone and 2-nonanone were absent. [m] Ap-

proximate yield of heptanoic acid 10%; 92% of hexyl groups accounted for. [n] Chlorocyclohexane. [o] Approximate heptanoic acid yields were 2% for first three runs, 8% for next three and 15% for the last; total hexyl groups accounted for about 88%. [p] Peroxide mole fraction 0.0065. [q] 0.009–0.010. [r] 0.0056. [s] Approximate heptanoic acid yields were 3, 4 and 11% in runs 1, 3 and 9; 85% of hexyl groups accounted for in these three runs.

TABLE II

RELATIVE SOLVENT REACTIVITIES TOWARD HYDROGEN ABSTRACTION BY 1-HEXYL FREE RADICALS USING CARBON TETRACHLORIDE AS THE REFERENCE (IN ORDER OF INCREASING REACTIVITY)[a]

Solvent	$\frac{(CCl_4)}{(SH)}$	10^2P [b]	Hexane [c]	1-Chlorohexane [c]	$\frac{k_H}{k_{Cl}}$ [d]	$k_{R\cdot}$ [e,f]	k_S [g]
Chlorobenzene	0	1.1	22	2	(0)		
	0.071	0.57	3	61			
	0.074	0.59	3	62			
Benzene	(See Table I)				(0)	1.0[e]	
Acetic acid	0.098	0.9	3	44	(0)		
Methyl acetate	.080	0.77	5	90	(0.002)		
	.14	1.1	4	91			
Ethyl acetate	.11	1.0	5	89	(.002)		
Methyl benzoate	.058	.47	4	36	(.002)		
t-Butyl alcohol	.121	1.1	6	67	(.004)		
	.180	1.5	4	53			
n-Butyl chloride	0	0.68	104	3	(.006)		0.04
	0.083	.65	11	107			
	.087	.68	..	101			
Toluene	(See Table I)				.006[h]	14[e]	
Cyclohexyl chloride	0.080	0.64	12	92	(.008)		
	.184	1.3	6	77			
Tetrahydrofuran	.10	0.90	13	74	(.01)		
	.094	0.85	11	88			
Acetone	(See Table I)				.010[h]	10,[e] 58[f,k]	5
Isoöctane[i]	0.265	1.0	8	88	(.013)	(20)[e]	
	.114	1.0	11	82			
Methanol	.098	0.90	9	24	(.02)	6[e]	
Cyclohexane	(See Table I)				(.02)[h]	20,[h] 9[h,l]	.024
Allyl alcohol	0.100	1.0	11	31	.024		1.5
	0.101	1.0	10	32			
Benzyl chloride	0	0.93	47	4	.028		1.6
	0.071	.57	20	47			
	.085	.67	18	52			
Dioxane	.102	.94	15	61	(.03)		0
	.060	.49	33	33			
2-Octene	.103	1.0	22	46	.051		
	.106	1.0	28	45			
1-Octene	.097	.9	19	28	.065	35,[i] 30[f,m]	
	.098	.9	22	26			
2-Butanol	.108	1.0	19	22	.084		
	.152	1.3	19	27			
Cyclohexene	.108	1.0	45	44	.10		
	.25	1.0	24	52			
2-Propanol	.253	1.0	20	36	.15	31[e]	
	.092	0.85	35	17			
Cyclohexanol	.119	1.0	16	6			
	.118	1.0	18	12			
Chloroform	(See Table I)				.40[h]	100[e]	.5
Isopropyl ether	0.132	1.2	66	15	.65	38[e]	
	0.098	1.0	80	10			
Carbon tetrachloride					[1.00][j]		90

[a] Heptanoyl peroxide was decomposed in the outgassed solvent mixture for 48 hours at 74°; the half-life is estimated to be about 3.5 hours.[1] [b] 100P is the mole per cent. of peroxide in the reaction mixture. [c] Mole per cent. of hexane and of 1-chlorohexane. [d] $k_H/k_{Cl} = (CCl_4)(\text{hexane} - 3)/(SH) \times (\text{1-chlorohexane})$; this assumes a "cage" hexane yield of 3%. The values in parentheses are probably good to a factor of two or three, the others to about 25%. [e] $k \times 10^{-6}$ mole^{-1} cc. sec.$^{-1}$ for methyl radical abstraction at 182° in the gas phase.[4] [f] $k \times 10^{-6}$ mole^{-1} cc. sec.$^{-1}$ for ethyl radical abstractions at 182° in the gas phase, calculated from parameters given by James and Steacie.[22] These values for methyl radicals and ethyl radicals are uncertain by a factor of about two. [g] Chain transfer constants for styryl radicals ($\times 10^4$) at 60°.[13] [h] See text. [i] 2,2,4-Trimethylpentane. [j] Reference compound. [k] Diethyl ketone. [l] Heptane. [m] 1-Hexene, 1-heptene.

hydrogen abstraction reactions from hydrocarbons by ethyl radicals in the gas phase.[6] Relative rates are available for a number of radicals in solution: the trichloromethyl radical,[7] the *t*-butoxy radical[8] and various peroxy radicals.[9] Mention may also be made of halogen atom reactivities.[10,11] In principle the chain transfer constants obtained in various polymer systems provide data for atom abstraction by a number of polymer radicals.[12]

The other major category of radical reactions, the radical addition reactions, have also been studied but will not be considered further here.[13]

However, quantitative data are lacking for most simple alkyl or aryl radicals. Only the methyl radical has been studied in solution.

Now that the reliability of diacyl peroxides as sources of alkyl radicals has been thoroughly established,[1,13c,14] it is possible to use these peroxides in quantitative studies in solution. The present work is concerned with the relative reactivity of various substrates in donating a hydrogen atom to the 1-hexyl free radical. Absolute rate constants are not yet available.

In our procedure the peroxide was decomposed in a solution containing a hydrogen donor, SH (such as acetone), and a halogen donor (such as carbon tetrachloride). If eq. 1 represents the only source of hexane, and eq. 2 the only source of

$$R\cdot + SH \xrightarrow{k_H} RH + S\cdot \qquad (1)$$

$$R\cdot + CCl_4 \xrightarrow{k_{Cl}} RCl + \cdot CCl_3 \qquad (2)$$

$$[RH]/[RCl] = k_H[SH]/k_{Cl}[CCl_4] \qquad (3)$$

1-chlorohexane, and if a very large excess of solvent is used, then it is easy to show that the relative hexane and 1-chlorohexane yields are given by eq. 3. If all of the concentration terms are measured, then the ratio k_H/k_{Cl} can be calculated. A repetition of the experiment with other substrates gives a corresponding ratio of rate constants for each. While the method does not give absolute rate constants, it does give useful tables of relative rates. In principle the procedure can as well be used to obtain relative rates for a series of halogen atom abstractions.

The technique of measuring radical reactions against a pilot reaction is very common. Gas phase methyl radical reactivities are measured against ethane formation, *t*-butoxy radical reactivities are measured against the decomposition of the *t*-butoxy radical into acetone, and so on. Edwards and Mayo were the first to employ halogen abstraction from carbon tetrachloride as the pilot reaction. They studied the reactivity of methyl radicals derived from acetyl peroxide.[5]

The present work consists of two parts. The first (*cf.* Table I) is a detailed study of the reaction of *n*-heptanoyl peroxide in five solvent mixtures to establish the scope, the limitations, and the validity of the procedure. The second (*cf.* Tables II and III) is a brief survey of the reactivity of about thirty representative compounds.

The Validity of the Procedure.—A detailed understanding of the mechanism of the decomposition of diacyl peroxides is not absolutely essential for use of the competition technique. But since peroxide reactions characteristically yield a spectrum of products, the reliability of the technique is enhanced by knowing the actual route to each product. Moreover, complex reactions of this type have a tendency to pursue unexpected paths. By determining several reaction products it is often possible to learn of such deviations and to allow for them.

Product studies of the reaction of *n*-heptanoyl peroxide in five solvent mixtures are summarized in Table I. The results supplement the related work on δ-phenylvaleryl peroxide.[14a,b] The absence of the cross termination product, 1,1,1-trichloroheptane, strengthens the hypothesis that the dodecane, the 1,1,1,3-tetrachloroheptane, and the *n*-hexyl heptanoate all stem directly or indirectly from geminate ("cage") reactions.[15] An induced mechanism for the formation of either the ester (RCOOR) or the dimer (RR) can be rigorously excluded in the δ-phenylvaleryl peroxide reactions since the yields are independent of peroxide concentration over a 200-fold variation. A mechanism of the type $R\cdot + (RCOO)_2 \rightarrow RCOOR + RCOO\cdot$ must involve either the three-halves or the second power of the peroxide concentration,[16] and the yields would have to increase with increasing peroxide concentration.

The only products due to statistically free radicals are therefore hexachloroethane, 1-chlorohexane and (in some reactions) hexane.

The originally plausible suggestion[5] that alkanes and alkyl chlorides are produced by a decarboxylative substitution step, eq. 4, has been shown to be without basis.[14c] Of course, if such a reaction occurred, diacyl peroxides would hardly be valid sources of free alkyl or aryl radicals. There is,

$$RCOO\cdot + CCl_4 \longrightarrow RCl + CO_2 + \cdot CCl_3 \qquad (4)$$

however, no evidence at the present time to support such a step and considerable evidence against it.[17]

It is essential to know all extraneous sources of hexane and of 1-chlorohexane (other than those given in eq. 1 and 2). One such source of hexane is disproportionation of 1-hexyl radicals. In the present systems this occurs only as a geminate radical reaction, for reactions with solvent effectively reduce the concentration of free 1-hexyl

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(6) D. G. L. James and E. W. R. Steacie, *Proc. Royal Soc.* (*London*), **244A**, 289 (1958).

(7) E. S. Huyser, This Journal, **82**, 391 (1960).

(8) A. L. Williams, E. A. Oberright and J. W. Brooks, *ibid.*, **78**, 1190 (1956).

(9) L. Bateman, *Quart. Revs.*, **8**, 147 (1954).

(10) Reviewed (a) in ref. 4b, p. 181; (b) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 347.

(11) G. A. Russell, This Journal, **80**, 4987 (1958).

(12) Reference 10b, p. 152.

(13) (a) Ref. 10b, p. 97; (b) J. Smid, A. Rembaum and M. Szwarc, This Journal, **78**, 3315 (1956); (c) J. Smid and M. Szwarc, *ibid.*, **78**, 3322 (1956), and earlier papers.

(14) (a) D. F. DeTar and C. Weis, *ibid.*, **79**, 3045 (1957); (b) **79**, 3041 (1957); (c) **78**, 4296 (1956).

(15) A detailed mechanism for δ-phenylvaleryl peroxide has already been presented.[14] The same mechanism applies to *n*-heptanoyl peroxide.

(16) *Cf.* C. G. Swain, W. H. Stockmayer and J. T. Clarke, This Journal, **72**, 5426 (1950).

(17) *Cf.* also H. J. Dauben, Jr., and L. L. McCoy, *ibid.*, **81**, 5404 (1959), footnote **27**.

radicals to negligible proportions. Reactions in solvent mixtures rich in carbon tetrachloride provide an estimate of the amount of geminate disproportionation, and it can be seen that the disproportionation:combination ratio is 2.8:19 or 0.15, the same as the gas phase value for ethyl radicals (0.14)[6] or 1-propyl radicals (0.13).[18]

A second extraneous source of hexane is by reaction of 1-hexyl radicals with a hydrogen donor (SH) other than the solvent SH component. This extraneous donor might be the peroxide itself, or the hydrogen-containing decomposition products. The effect would be to make the k_H/k_{Cl} ratio too large The data in Table II, particularly the very low k_H/k_{Cl} values, provide good evidence against this possible complication.

There is yet another complication which has been reported previously.[19] With certain solvents, notably cyclohexane, there is an efficient peroxide-induced cross-transfer reaction which converts much of the solvent into chloroform and chlorocyclohexane. Since chloroform is a very good

$$\cdot CCl_3 + C_6H_{12} \longrightarrow CHCl_3 + \cdot C_6H_{11} \qquad (5)$$

$$\cdot C_6H_{11} + CCl_4 \longrightarrow C_6H_{11}Cl + \cdot CCl_3 \qquad (6)$$

hydrogen-donor and a very poor chlorine-donor, the yield of hexane is much higher than warranted by the reactivity of cyclohexane itself toward 1-hexyl radicals. This effect explains one of the deviant results reported by Edwards and Mayo.[5,4]

As for the reactivity of chlorine-donors, complications might arise from the various chlorine-containing species such as 1-chlorohexane, 1,1,1,3-tetrachloroheptane and hexachloroethane. The former two are much less reactive than carbon tetrachloride, and hexachloroethane is of about the same reactivity.[20]

We conclude that the reliability of the competitive method has now been established.

Results.—Certain special features of the reactions reported in Table I may now be considered. Apparently 1-hexyl radicals do not add to benzene in competition with abstracting chlorine from carbon tetrachloride, for the yield of 1-chlorohexane is essentially independent of solvent composition. Addition to benzene should reduce the yield in solvent mixtures containing high fractions of benzene. The cause of the progressively lower hexachloroethane yields as the mole fraction of benzene is increased has not been determined. It is possible to show by detailed analysis that addition of trichloromethyl radicals to benzene could account for the result with reasonable values for the rate constants, but product corroboration has not yet been obtained.

In toluene the slight increase in hexane yields in solutions containing high mole fractions of toluene indicates some hydrogen abstraction, almost certainly from the methyl side chain. Allowance is made for hexane derived from geminate disproportionation of hexyl radicals by subtracting 2.8 from observed hexane yields. The relative reactivity k_H/k_{Cl} = [(hexane)−2.8](CCl$_4$)/(1-chlorohexane)(toluene) = 0.006. This represents an order of magnitude estimate.

The results in acetone–carbon tetrachloride mixtures differ somewhat from those in the other four solvents. Since some 92% of the peroxide fragments have been identified, only part, if any, of this difference can be charged to induced peroxide decomposition. Tentatively we conclude that the geminate radical reactions are less important than in the other solvents although there is no obvious explanation for this. The value of k_H/k_{Cl} = (hexane − 3.4)(CCl$_4$)/(1-chlorohexane)(acetone) = 0.010 based on the last three runs with the highest acetone fractions.

The radical-induced exchange reaction in cyclohexane–carbon tetrachloride mixtures complicates the analysis of the results. An exact solution of the equations appears to be impractical, but an approximate solution is possible in terms of average values of the concentrations. Thus [(hexane) − 3]/(1-chlorohexane) = $k_H(C_6H_{12})/k_{Cl}(CCl_4)$ + $k_H'(CHCl_3)/k_{Cl}(CCl_4)$. In this expression the concentration of chloroform is taken as half its final value, the concentration of carbon tetrachloride is the initial value less half the final chloroform concentration, k_H is the rate of abstraction of hydrogen from cyclohexane and k_H' the rate of abstraction of hydrogen from chloroform. Further, it is assumed that the hydrogen atoms of chlorocyclohexane are of essentially the same reactivity as those of cyclohexane, and that the chlorine atoms of chloroform and of chlorocyclohexane are essentially inert toward the hexyl radicals. The value of k_H'/k_{Cl} = 0.38 is derived below from the runs in chloroform. The hexane yield from geminate disproportionation of hexyl radicals is taken as 3 mole per cent. Except for the last two runs the results are correlated well using k_H/k_{Cl} = 0.02 (see Table IV).

With chloroform the possibility of abstracting a halogen atom from the chloroform must be

TABLE III

RELATIVE REACTIVITIES OF 1-HEXYL FREE RADICALS TOWARD HALOGEN ABSTRACTION AND HYDROGEN ABSTRACTION[a]

Solvent system	$\frac{[SCl]}{[S'H]}$	Hexane	1-Chlorohexane	$\frac{k_H}{k_{Cl}}$
C_2Cl_6	0.029	67	10	0.33[b]
$CHCl_3$	.043	74	13	
$CF_2ClCFCl_2$	.11	36	2	(2)[c]
$C_6H_5CH_3$	.13	36	2	
$CF_2ClCFCl_2$	.12	16	7	(0.25)
C_6H_6	.13	17	7	
$CF_2ClCFCl_2$	.14	58	4	(2)[c]
Cyclohexane				

[a] Conditions the same as reported Tables I and II. [b] Calculated from (RCl)/(hexane-3) = $k_{Cl}'/k_H + k_{Cl}(CCl_4)/k_H(CHCl_3)$ using k_{Cl}'/k_H = 0.060. See text concerning reactions in chloroform–carbon tetrachloride mixtures for derivation and definition of terms. The relative reactivity toward chlorine abstraction is C_2Cl_6:CCl_4 = 0.38/0.33 = 1.2 (est. accuracy about 50%). [c] The relative chlorine abstraction rates are $CF_2ClCFCl_2$:CCl_4, about 0.01.

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(18) J. W. Kraus and J. G. Calvert, THIS JOURNAL, **79**, 5921 (1957).

(19) *Cf.* J. P. West and L. Schmerling, *ibid.*, **72**, 3525 (1950).

(20) *n*-Butyl bromide gives no significant amount of 1-bromohexane, nor does benzyl chloride give appreciable 1-chlorohexane.[21] As for the 1,1,1,3-tetrachloroheptane, its yield is not reduced at low carbon tetrachloride ratios, conditions under which its reaction with 1-hexyl radicals is most favored.

(21) D. F. DeTar and R. Culbertson, unpublished results.

(22) D. G. L. James and E. W. R. Steacie, *Proc. Royal Soc.* (*London*), **244A**, 297 (1958).

Table IV

Additional Data for Carbon Tetrachloride–Cyclohexane Mixtures[a]

$(C_6H_{12})_0$[b]	$(CCl_4)_0$[b]	$(CHCl_3)_f$[c]	(CCl_4)av.[d]	$\frac{(RH) - 3}{(RCl)}$[e] Obsd.	Calcd.
1.91	8.25	0.54	7.98	0.017	0.009
2.68	7.41	.72	7.05	.026	.028
4.21	7.11	.88	6.67	.035	.037
4.90	4.90	.90	4.45	.063	.061
6.20	3.39	1.06	2.86	.108	.113
7.21	2.31	1.26	1.68	.135	(.22)
7.50	1.98	1.36	1.30	.120	(.32)

[a] See Table I for the rest of the data for these runs. [b] Initial concentrations (moles/liter). [c] Final concentration. [d] Average concentration = $(CCl_4)_0 - (CHCl_3)_f/2$. [e] $[(RH) - 3]/(RCl) = 0.02(C_6H_{12})/(CCl_4 + 0.38\ CHCl_3)/(CCl_4)$.

allowed for. Since $d(RCl)/dt = k_{Cl}'(CHCl_3) + k_{Cl}(CCl_4)$ and $d(RH)/dt = k_H(CHCl_3)$, $d(RCl)/d(RH) = (RCl)/(\text{hexane} - 3) = k_{Cl}'/k_H + k_{Cl}(CCl_4)/k_H(CHCl_3)$ where k_{Cl}' is the rate constant for halogen abstraction from chloroform and (hexane −3) is the total hexane less 3% arising from the geminate reaction. There is some problem as to the best way to evaluate the data, but the runs in chloroform and in 0.058 mole fraction carbon tetrachloride seem to be the best for finding k_{Cl}'/k_H, while the runs using $(CCl_4)/(CHCl_3) = 2.87$, 1.74 and 1.00 seem to be best for the other ratio. By using these sets of data, $k_{Cl}'/k_H = 0.060$ and $k_{Cl}/k_H = 2.6$. The former value is considered reliable to about 30%, the latter to about 10%. The value of $k_{Cl}'/k_{Cl} = 0.02$ for chlorine abstraction from chloroform relative to carbon tetrachloride.

Applying the same equation to the comparison between chloroform and hexachloroethane (Table III) gives a k_{Cl}/k_H ratio for this system of 3.0. Thus hexachloroethane is about as reactive as carbon tetrachloride. On the other hand, 1,1,2-trichlorotrifluoroethane is much less reactive. The k_H/k_{Cl} values here compared with those in Table II indicate that these halogens are 0.003-0.01 as reactive as those of carbon tetrachloride.

The data from the results of the solvent survey are reported in Table II. In the column headed k_H/k_{Cl} are summarized all of the relative reactivities measured in this work. The values in parentheses are reliable to within a factor of perhaps two or three. The other values are perhaps good to about 25% relative. The error limits appear to be comparable to those reported in other work.[4,6] The extent of extraneous reactions has not yet been examined for most of these systems. Except for the last six compounds in the table, carbon tetrachloride is almost too reactive to serve as a good reference compound. While it is possible to use quite low carbon tetrachloride concentrations, to do so also introduces serious problems in that it aggravates the importance of the various side reactions already discussed and perhaps of others not considered. We have been exploring the use of other halogen donors as reference solvents, but those tested so far are either of the same reactivity as carbon tetrachloride or else almost too unreactive.

We were interested in the possible conversion of the 1-hexyl radical to the 2-hexyl radical by an intramolecular chain transfer reaction. This could be detected by observing the yield of 2-chlorohexane into which the 2-hexyl radical should be converted. There is, however, no evidence for as much as 3 mole per cent. of 2-chlorohexane in the several runs examined for this product. The reaction of the 1-hexyl radical with carbon tetrachloride (eq. 13) wins out over intramolecular hydrogen abstraction.

Discussion.—The reactivities of various compounds toward hydrogen abstraction by the 1-hexyl radical may be compared with similar data for the methyl radical. The values for the rate constants for methyl radical hydrogen abstraction in the gas phase are given in the next to the last column of Table II. In general there is at least qualitative agreement. A plot of log k_{CH_3} *vs.* log k_H/k_{Cl} gives points which scatter somewhat about a straight line. Using the most reliable data based on acetone, 2-propanol, 1-octene, chloroform and isopropyl ether, the line has a slope of 0.4. However, the reactivity of isopropyl ether toward 1-hexyl radicals is suspiciously high; if this is disregarded, the slope of the line is about 0.6. About all that can be concluded from the present data is that 1-hexyl radicals show the same general dependence on structure of SH as do methyl radicals, but that they are considerably more selective. For a series of compounds toward which methyl radical reactivities cover a range of 100, 1-hexyl radical reactivities may be expected to cover a range of 10,000.

It is not clear just how to interpret the data for gas phase ethyl and methyl radical reactivities. The methyl radical reactivity data appear to be limited for the most part to series of individual runs, at best using several methyl radical sources. Such data show very considerable scatter. The ethyl radical data were deliberately taken with from ten to thirty runs on each of a limited series of hydrocarbons. Individual rates are not generally explicitly given, but instead Arrhenius parameters or their equivalents are tabulated. This procedure is no doubt justified by the relatively large scatter of the rate data, but it does tend to obscure trends in rates among related series of compounds of the sort involved in the data of Table II. For the very limited data available calculated rates of methyl radical reactivities appear to be the same as those for ethyl radical reactivities (for secondary saturated hydrogen atoms, for secondary allylic hydrogen atoms, for secondary hydrogen atoms alpha to acetylenic bond and to a ketone) in spite of apparently erratic though considerable variation of activation energies and *A*-factors. More extensive and more accurate data would be most welcome, though the labor involved in obtaining these will be very great indeed.

It is possible to make comparisons with the chain transfer constants for polymerization reactions.[12,23] The values for styryl radicals are given in the last column of Table II. There are many parallels, but there are also discrepancies. Since the chain transfer of styrene with bromobenzene and perhaps with other aromatic com-

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(23) R. A. Gregg and F. R. Mayo, This Journal, **75**, 3530 (1953).

pounds has some strange features,[24] it appears to be necessary to postpone consideration of aromatic compounds until other data become available. In fact the chain transfer constants do not seem to fit in very well with the data for methyl radicals and 1-hexyl radicals. Since styryl radicals are substituted benzyl radicals, they should be much less reactive and much more selective than 1-hexyl radicals. Yet the total reactivity range toward hydrogen abstraction from cyclohexane to chloroform (excluding dioxane) is only a factor of 20, while for methyl radicals from acetone to chloroform the factor is 10 and for 1-hexyl radicals from acetone to chloroform the factor is 40. In our opinion the understanding of these discrepancies must await further work on the reactivities of simple radicals.

Acknowledgment.—We wish to express our appreciation to the National Science Foundation and to the Research Committee of the University of South Carolina for grants which made possible the purchase of equipment for gas chromatography. We also wish to acknowledge our indebtedness to Dr. Robert C. Lamb for his preliminary investigation of the reaction of *n*-heptanoyl peroxide with carbon tetrachloride.

Experimental

Reagents and Reference Compounds.—The following commercial samples were redistilled and subjected to additional purification as indicated. The infrared spectra were examined for identity and gross impurity, and the amount of trace impurity checked by gas chromatography; the amount of such impurity was often less than 0.5% and in the following list was less than 1% unless another limit is stated: 1-chlorohexane, *n*-dodecane, *n*-hexane, 1-hexene, chloroform chlorobenzene, chlorocyclohexane, benzyl chloride, chloroacetone (3%), acetonylacetone (2%), carbon tetrachloride (alkali and acid washed, dried, and passed through F-20 alumina of activity grade I),[25] cyclohexane, toluene (2%), benzene, acetone, methanol, 2-propanol, 2,2,4-trimethylpentane, cyclohexene, dioxane (passed through F-20 alumina of activity grade I), ethyl acetate, acetic acid, isopropyl ether (alumina), *n*-butyl ether (alumina), allyl alcohol (K_2CO_3, and distilled with carbon tetrachloride),[26] tetrahydrofuran (alumina), 2-octene (alumina), 2-butanol (2%), cyclohexanol, *t*-butyl alcohol, 1-octene, 1,1,2-trichlorotrifluoroethane, methyl acetate. 2-Chlorohexane and 3-chlorohexane of better than 99% purity were prepared from the corresponding alcohols with hydrochloric acid and zinc chloride.

1,1,1,3-Tetrachloroheptane[27,28] was obtained in a 33-g. yield from the reaction of 26 g. of 1-hexene, 154 g. of carbon tetrachloride and 4.8 g. of benzoyl peroxide at reflux temperature for 4 hours. In order to obtain pure material it was necessary to pass the crude product through F-20 alumina to remove an impurity with a carbonyl (ester) group. The pure material had a b.p. of 86–87° (uncor.) at 6 mm., $n^{20}\text{D}$ 1.4775. Analysis by gas chromatography showed the presence of about 3% of impurities.

Anal. Calcd. for $C_7H_{12}Cl_4$: C, 35.3; H, 5.1; Cl, 59.6. Found: C, 35.5; H, 5.2; Cl, 59.5.

***n*-Hexyl *n*-heptanoate**[27,29] was prepared by direct esterification, b.p. 143–145° at 24 mm., 2% impurities by gas chromatography.

1,1,1-Trichloroheptane was prepared by portionwise addition of a total of 4 g. of benzoyl peroxide to a refluxing mixture of 98 g. of 1-hexene and 650 ml. of chloroform (nitrogen atmosphere) over a period of 2 weeks. By distillation 48 g. of product, b.p. 75–80° at 7 mm., was obtained. A small amount of ester impurity was removed by passing the liquid through neutral alumina of activity grade I, and an impurity with a longer retention time was removed by fractionation under a controlled pressure of 6 mm. (b.p. 65°), $n^{25}\text{D}$ 1.4560, estimated impurities less than 0.5%, yield 35 g.

Anal. Calcd. for $C_7H_{13}Cl_3$: C, 41.30; H, 6.44; Cl, 52.26. Found: C, 41.6; H, 6.5; Cl, 52.0.

A mixture of 0.96 g. of the 1,1,1-trichloroheptane was heated with 5 ml. of concd. sulfuric acid for 2 hours at 50–60° and for 6 hours longer at 80–90°. By extraction of the diluted reaction mixture with ether 0.36 g. (60%) of an acid was obtained, $n^{25}\text{D}$ 1.4210 (commercial *n*-heptanoic acid had $n^{25}\text{D}$ 1.4215), and with an infrared curve identical to that of the commercial acid.[30]

N-Heptanoyl Peroxide.—A solution of 104 g. (0.70 mole) of redistilled *n*-heptanoyl chloride (from the acid by treatment with thionyl chloride) in 300 ml. of anhydrous ether was added during a period of 45 minutes to a stirred solution of 113 g. (1.4 moles) of sodium peroxide dissolved in 1 l. of ice-water. The temperature was maintained at 0–2°. After an additional hour at 3–5°, the ether layer was separated and washed with cold water, with sodium bicarbonate solution, and again with water. After drying over magnesium sulfate, the ether was removed *in vacuo* and then in a slow air stream. This gave 75 g. of liquid peroxide with a titer of 97.6 ± 0.5% (80% yield).

Procedure for the Peroxide Decompositions.—Peroxide solutions were made up by weight in rubber-capped vials. They were then transferred to decomposition vials of 15–20-ml. volume. The solutions were outgassed three times on a vacuum manifold, with intermediate flushing with high purity nitrogen. They were then sealed under vacuum and heated at 74° for 48 hours. The solutions were then stored at −20° until analyzed. Analyses were performed by gas chromatography using for the most part a Perkin–Elmer model 154 Vapor Fractometer, but for a few series a model 119 unit from the F and M Scientific Glassware Co.[31] The reaction solution was analyzed directly without preliminary treatment using 20-μl. samples. A large number of solutions was analyzed with one setting of the instrument in a continuous series of determinations. Samples were run in a randomized order and standard solutions were interspersed. Many different columns were used. Details of the procedures may be obtained by consulting the Ph.D. thesis of D. V. Wells, but some typical examples are:

Hexane in benzene and carbon tetrachloride mixtures was determined on a 2 meter by 6 mm. column containing firebrick coated with polyethylene glycol 1500, column temp. 65°, helium carrier at 0.6 atm. and flow rate 40 ml. per minute. Retention times were air 1.3 min., hexane 1.6, 1-hexene 1.8, carbon tetrachloride 4.5, benzene 7.9 and chloroform 9.8. Standard samples of hexane ($6–70 \times 10^{-4}$ *M*) were made up in 0.5:0.5 mole fraction benzene and carbon tetrachloride. Four other columns were also used successfully including 2-ethylhexyl sebacate in series with Tide (a commercial household detergent containing sodium sulfate, a sulfonated kerosene–aromatic alkylate, and other ingredients), and a 1-meter 2-ethylhexyl sebacate column in series with a 1-meter tetramethylene glycol dimethyl ether column.

1-Chlorohexane was determined on a 1-meter column of polyethylene glycol 1500 in series with a 1-meter column with didecyl phthalate, temp. 122°, press. 0.6 atm., helium flow rate 56 ml. per min. Retention times were for carbon tetrachloride 1.9 min., benzene 2.3, 2-chlorohexane 4.6, 1-chlorohexane 6.1, chlorobenzene 8.6. 1-Chlorohexane standards ($2–14 \times 10^{-2}M$) were run in a 0.5:0.5 mole fraction carbon tetrachloride–benzene mixture. No peaks were found at either 4.6 min. (2-chlorohexane) nor at 8.6 min. (chlorobenzene); 0.03 mole per mole of peroxide would have given a definite peak. Other columns were used successfully in other runs.

Dodecane and hexachloroethane were determined on a 1.2-meter column with Dow–Corning high vacuum silicone grease

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[24] F. R. Mayo, This Journal, **75**, 6133 (1953).

[25] *Cf.* H. Brockmann and H. Schodder, *Ber.*, **74**, 73 (1941). F-20 alumina is the designation of the Aluminum Ore Co. for an alkaline alumina of chromatography grade. The activity has been checked by use of the dye mixtures of Brockmann and Schodder.

[26] O. Kamm and C. S. Marvel, "Organic Syntheses," Coll. Vol. I, 2d ed., John Wiley and Sons, Inc., New York, N. Y., 1941, p. 43.

[27] By Dr. R. C. Lamb.

[28] Procedure of M. S. Kharasch, E. V. Jensen and W. H. Urry, This Journal, **69**, 1100 (1947).

[29] H. Rheinholt, O. König and R. Otten, *Ann.*, **473**, 258 (1929).

[30] *Cf.* H. J. Prins, *J. prakt. Chem.*, **89**, 414 (1914).

[31] The prototype is described by S. dal Nogare and L. W. Safranski, *Anal. Chem.*, **30**, 894 (1958).

at 156° and a flow rate of 60 ml. per min. Retention times were for carbon tetrachloride 0.6 min., *n*-heptanoic acid 4.0, hexachloroethane 4.8, 1,1,1-trichloroheptane 6.2, dodecane 7.5, 1,1,1,3-tetrachloro-heptane 12.0 and hexyl heptanoate 25.7.

1,1,1,3-Tetrachloroheptane was determined on a 1-meter column with silicone oil 200 in series with a 1-meter Tide column, 182°, 1.1 atm., 45 ml. per min. Retention times were for cyclohexane 1.5 min., benzene 2.7, hexachloroethane 6.6, 1,1,1-trichloroheptane 7.5, dodecane 8.6, 1,1,1,3-tetrachloroheptane 15.0. Some samples showed a small peak at 6.2 min. in the former or at 7.5 min. in the latter system (1,1,1-trichloroheptane), but the amount was never more than 0.03 mole per mole of peroxide.

n-Hexyl *n*-heptanoate was determined on a 1-meter column of Dow-Corning silicone oil 550, temp. 245°, press. 0.7 atm., 45 ml. per min. Retention times were for carbon tetrachloride 0.4 min., hexachloroethane 1.0, dodecane 1.2, *n*-hexyl *n*-heptanonate 2.7.

In general it was not practical to make up standards in all solvent mixtures encountered. However, a large variety of standard solutions was employed, and the solvents did not usually show any appreciable effect on the peak area–concentration relationship.

In this work products were identified only on the basis of the retention time, but always in comparison with authentic samples of the compound (often on a series of columns) and by chemical reasonableness. From large scale runs in carbon tetrachloride the following compounds were isolated physically (moles per mole of peroxide are given in parentheses): CO_2 (1.62), 1-chlorohexane (1.0), dodecane (same), *n*-hexyl *n*-heptanoate (0.2), hexachloroethane (0.15), 1,1,1,3-tetrachloroheptane (0.1), and *n*-heptanoic acid (0.1).[27] Errors will tend to be those of overestimating the amount of a component by failure to recognize contamination by an unknown of similar retention time. Errors of selective underestimation are less likely.

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Chemical Shifts in $C_5H_5^-$, C_6H_6 and $C_7H_7^+$; Chemical Shifts and π-Electron Densities[1]

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The chemical shifts of several salts and derivatives of the cyclopentadienyl anion $C_5H_5^-$ and the tropylium cation $C_7H_7^+$ have been determined relative to benzene as an internal standard in dimethyl sulfoxide and acetonitrile. The observed shifts are +1.85 and −1.9 p.p.m. for $C_5H_5^-$ and $C_7H_7^+$, respectively. These shifts are mainly accounted for by the electrostatic interaction between charge localized in the π-orbital of a carbon atom and the electrons in the C–H bond. The results, in conjunction with their theoretical interpretation, are used to determine "experimental" charge distributions in other aromatic systems.

Introduction

The π-electron density on the carbon atoms of conjugated molecules has an important effect on ring-proton chemical shifts[4]; however, in most organic compounds other factors such as ring currents[5–8] and the magnetic anisotropy of neighbors[9–11] are of great significance. In practice these three effects are not easily distinguished from one another.

In the isoelectronic series cyclopentadienyl anion $C_5H_5^-$, benzene C_6H_6 and tropylium cation $C_7H_7^+$,[12–14] each molecule has six π-electrons to contribute to the ring current, and the radii of the rings are so similar that the resulting screening[5] is, in every case, almost the same. Therefore, the relative hydrogen shifts in a *common solvent* should be almost entirely due to the different electron densities; moreover the π-electron densities in these species are known by their symmetry.

The total shifts were first determined by Leto, Cotton and Waugh[15] relative to an external standard in three different solvents. These values have now been measured in two common solvents, and the origin of the chemical shifts in these species and other aromatic compounds has been investigated theoretically. An electrostatic model has been derived that, in the main, accounts for our results and can be used to determine charge distributions in other aromatic molecules.

Experimental

Chemicals.—Acetonitrile, b.p. 82°, was distilled from phosphorus pentoxide. Dimethyl sulfoxide (Stephen Chemical Co., Chicago, Ill.) was dried by passage through a column of Linde molecular sieve powder. Tetrahydrofuran (Matheson) was treated with potassium hydroxide, refluxed, and distilled at 66° from lithium aluminum hydride and stored in an atmosphere of nitrogen in the refrigerator. Dicyclopentadiene (Enjay Co., New York) was cracked at 210° and the cyclopentadiene distilled, b.p. 42°, immediately before use. Ferrocene was kindly supplied by du Pont. Ruthenocene and osmocene were prepared by E. Alexander Hill, III.

Cyclopentadienylsodium.[16]—Equimolar quantities of cyclopentadiene and sodium sand were stirred in tetrahydrofuran under a nitrogen atmosphere at room temperature to produce an intensely purple solution of cyclopentadienylsodium.

Cyclopentadienyllithium.[17]—Cyclopentadiene was treated with an equimolar amount of phenyllithium in ether at 0° under an atmosphere of helium. The white precipitate was filtered and washed twice with ether and dried under helium.

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