900. *The Reactions of Phenyl Radicals from the Photolysis of Acetophenone and the Strength of the* C–H *Bond in Benzene.*

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The photolysis of acetophenone has been shown to be a convenient source of phenyl radicals whose rates of reaction with acetophenone, methane, cyclopropane, and isobutane have been measured. D(Ph–H) equals 102 kcal./mole.

The reactions of phenyl radicals in solution have been extensively investigated, particularly by Hey and his co-workers. No full kinetic study in the gas phase has been reported, probably because no convenient source of phenyl radicals was developed and because the necessary analyses were almost impossible without gas chromatography.

It was expected, by analogy with acetone, that the photolysis of acetophenone could be satisfactorily described by the following series of reactions:

$$\mathrm{Ph{\cdot}CO{\cdot}Me} + h\nu \longrightarrow \mathrm{Ph} + \mathrm{CO} + \mathrm{Me} \qquad (1)$$

$$\mathrm{Ph} + \mathrm{Ph{\cdot}CO{\cdot}Me} \longrightarrow \mathrm{PhH} + \mathrm{R} \qquad (2)$$

$$2\mathrm{Ph} \longrightarrow \mathrm{Ph{\cdot}Ph} \qquad (3)$$

$$\mathrm{Me} + \mathrm{Ph{\cdot}CO{\cdot}Me} \longrightarrow \mathrm{CH_4} + \mathrm{R} \qquad (4)$$

$$2\mathrm{Me} \longrightarrow \mathrm{C_2H_6} \qquad (5)$$

$$\mathrm{Me} + \mathrm{Ph} \longrightarrow \mathrm{PhMe} \qquad (6)$$

The detection of benzene, toluene, biphenyl, methane, and ethane among the products was in agreement with this general scheme. When acetone is photolysed both methyl and acetyl radicals are first formed, as can be shown by the detection of products of acetyl at low temperatures. No signs that acetone yields acetyl can be found at temperatures as high as 250°; there is, therefore, no reason to write reaction (1) as a series of steps in this instance. Some evidence was found that the yield of products decreased at high pressures. The decrease was probably caused by the collisional deactivation of excited acetophenone molecules, but no precise actinometric work was done so that for the present purpose reaction (1) suffices. The nature of the radicals, R, is not known. Mixtures are presumably formed. It is only necessary to postulate that these radicals do not directly form any of the significant products.

Benzene and biphenyl could have been formed by reactions of the photolytically activated acetophenone that do not involve phenyl radicals as an intermediate. The results for the rate of formation of benzene and biphenyl when acetophenone (approx. 10^{-6} mole cm.$^{-3}$) is photolysed at 330° in the presence of nitric oxide show that the additive acts as if the products came solely from phenyl radicals. Accordingly the rate of formation of benzene can be written:

$$R_{\mathrm{PhH}} = k_2[\mathrm{Ph}][\mathrm{Ph{\cdot}CO{\cdot}Me}]$$

and that of biphenyl

$$R_{\mathrm{Ph{\cdot}Ph}} = k_3[\mathrm{Ph}]^2.$$

Similar equations were derived to describe the formation of methane and ethane in the photolysis of acetone and are applicable also to the products of methyl radicals from acetophenone. Biphenyl is, however, also produced by the reaction:

$$\mathrm{Ph} + \mathrm{Ph{\cdot}CO{\cdot}Me} \longrightarrow \mathrm{Ph{\cdot}Ph} + \mathrm{CO{\cdot}Me} \qquad (7)$$

Hence, from a steady-state treatment

$$\frac{R_{\mathrm{Ph{\cdot}Ph}}}{R_{\mathrm{PhH}}} = \frac{k_3}{k_2{}^2}\cdot\frac{R_{\mathrm{PhH}}}{[\mathrm{Ph{\cdot}CO{\cdot}Me}]^2} + \frac{k_7}{k_2}$$

A plot of ($R_{\mathrm{Ph{\cdot}Ph}}/R_{\mathrm{PhH}}$) against ($R_{\mathrm{PhH}}/[\mathrm{Ph{\cdot}CO{\cdot}Me}]^2$) should be a straight line of slope $k_3/k_2{}^2$ and intercept k_7/k_2. Plots of this type were first obtained by the addition of nitric oxide to acetophenone at 327°. The points lay roughly on a line but the scatter was large. Work was subsequently confined to variations of the acetophenone concentration. The results are given in Table 1 and plotted in Fig. 1. The values of k_2 and k_7 are:

Temp. (°K)	550	599	615	680
$10^{-8}k_2$ (mole^{-1} cm.^{3} sec.$^{-1}$)	15·7	29·3	23·7	44·4
$10^{-8}k_7$ (mole^{-1} cm.^{3} sec.$^{-1}$)	0·15	0·29	0·23	0·44

From these figures, the values of the A factors and activation energies listed in Table 3 have been calculated on the assumption that log k_3 (mole^{-1} cm.^{3} sec.$^{-1}$) = 14 and that $E_3 = 0$. There is no evidence for this assumption; it is made to facilitate the presentation of the results and their comparison with those for other radicals.

Values for the rate constant for the attack of methyl radicals on acetophenone have been obtained from the rates of formation of methane and ethane found in the runs and the equation

$$k_4 = k_5{}^{\frac{1}{2}}(R_{\mathrm{MeH}}/R_{\mathrm{Me{\cdot}Me}}{}^{\frac{1}{2}}[\mathrm{Ph{\cdot}CO{\cdot}Me}]).$$

k_5 has been taken as $10^{13\cdot35}$ mole^{-1} cm.^{3} sec.$^{-1}$.[1] The results are plotted in Fig. 2 from which

$$\log k_4\ (\mathrm{mole^{-1}\ cm.^3\ sec.^{-1}}) = 10{\cdot}7 - (7400/2{\cdot}3\boldsymbol{R}T).$$

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[1] Shepp, *J. Chem. Phys.*, 1956, **34**, 939.

TABLE 1.

Products of the photolysis of acetophenone.

Temp.	10^6[A]	Time	CO	PhH	Ph·Ph	Ph·Me	CH_4	C_2H_6	
(°K)	(mole cm.$^{-3}$)	(sec.)		(10^{-12} mole c.c.$^{-1}$ sec.$^{-1}$)					log k_4
557	1·14	120	114	38·2	0·838	0·729	7·89	24·0	7·433
552	1·17	120	120	40·7	0·875	0·745	7·75	25·0	7·293
549	1·17	120	107	35·6	0·667	0·604	7·29	19·4	7·319
549	1·18	120	90·9	37·4	0·755	—	15·0	35·8	7·497
553	1·39	120	116	42·7	0·859	0·818	9·37	21·6	7·331
549	1·42	120	96·1	38·5	0·693	0·585	13·4	22·3	7·469
548	1·76	120	82·5	37·8	0·516	0·641	12·5	20·8	7·362
550	1·78	120	—	42·5	0·663	0·886	—	—	—
558	2·17	120	—	45·3	0·588	0·990	—	—	—
550	2·57	120	—	37·6	0·466	0·865	—	—	—
595	0·774	30	—	69·7	1·53	1·21	—	—	—
597	0·792	60	145	64·4	1·47	1·56	15·2	33·9	7·689
592	0·965	60	—	64·7	1·29	0·82	—	—	—
599	1·09	60	192	68·8	1·04	1·63	23·9	34·6	7·741
597	1·32	60	173	77·3	1·22	1·43	23·4	50·5	7·567
599	1·41	60	184	72	1·07	1·68	24·8	35·3	7·641
597	1·72	60	—	72	1·07	1·71	—	—	—
602	2·01	60	189	93	1·07	1·24	30·8	26·7	7·642
614	1·06	60	—	82·9	1·93	1·49	—	—	—
614	1·26	60	199	95·4	1·93	1·77	35·2	60·2	7·724
614	1·49	60	198	105	1·89	2·18	36·0	35·0	7·783
616	1·57	60	195	97·9	1·49	2·49	43·1	79·6	7·658
619	2·31	60	—	111	1·33	—	—	—	—
618	2·31	60	—	99	1·28	2·39	—	—	—
618	3·07	70	257	119	1·45	2·68	31·1	44·8	7·665
683	0·951	30	—	129	1·70	3·13	—	—	—
678	0·984	30	—	134	2·52	3·13	—	—	—
675	1·03	30	253	131	2·17	3·35	40·6	42·7	7·949
681	1·04	30	189	103	2·04	3·35	38·3	35·5	7·963
676	1·04	30	247	128	2·10	3·07	28·9	39·8	7·664
666	1·05	30	245	129	2·10	3·50	57·3	46·7	8·071
664	1·13	30	—	130	2·08	2·71	—	—	—
666	1·14	30	249	116	1·33	2·56	51·2	40·2	8·022
669	1·35	30	—	135	2·00	3·50	—	—	—
679	1·39	30	317	138	1·91	3·81	67·7	35·6	8·090
685	1·83	30	303	149	1·83	4·60	67·4	43·6	7·917
671	1·92	30	235	118	0·99	2·77	54·6	26·8	7·909
684	3·16	60	298	163	1·02	3·83	76·8	25·0	7·865

[A] is the concentration of acetophenone.

TABLE 2.

The reaction of phenyl radicals with methane.

Temp.	[A]	[CH_4]	Time	PhH	Ph·Ph	Ph·Me	
(°K)	(10^{-6} mole cm.$^{-3}$)		(sec.)	(10^{-12} mole c.c.$^{-1}$ sec.$^{-1}$)			log k
561	1·16	2·39	120	42·7	0·82	—	7·622
561	1·17	3·60	120	40·3	0·72	0·86	7·623
557	1·15	4·19	120	38·6	0·72	0·74	7·511
557	1·17	6·51	120	39·3	0·68	0·96	7·545
600	1·08	2·76	60	73·8	1·36	—	7·865
599	1·09	3·84	60	75·5	1·34	—	7·907
596	1·09	5·78	60	72·1	1·20	1·48	7·866
596	1·10	6·46	60	78	1·28	1·62	7·903
691	0·929	1·41	30	146	2·06	3·10	8·506
692	0·946	1·91	30	140	2·06	4·19	8·408
694	0·939	3·09	35	146	2·02	3·77	8·381
688	0·956	3·31	30	146	2·10	4·19	8·271
692	0·925	5·04	30	151	1·79	—	8·467
697	0·930	5·71	30	156	1·83	3·04	8·425

[A] is the concentration of acetophenone.

The Reaction of Phenyl Radicals with Hydrocarbons.—When methane is added to the system, benzene is also formed by the reaction:

$$\mathrm{Ph + MeH \longrightarrow PhH + Me} \qquad (8)$$

The rate of reaction of phenyl radicals with methane was calculated from the results in Table 2 after proper allowance had been made for the formation of benzene by abstraction of hydrogen from acetophenone. From rate constants plotted in Fig. 2, it is found that

$$\log k_8\ (\text{mole}^{-1}\ \text{cm.}^3\ \text{sec.}^{-1}) = 11{\cdot}9 - (11100/2{\cdot}3\boldsymbol{R}T).$$

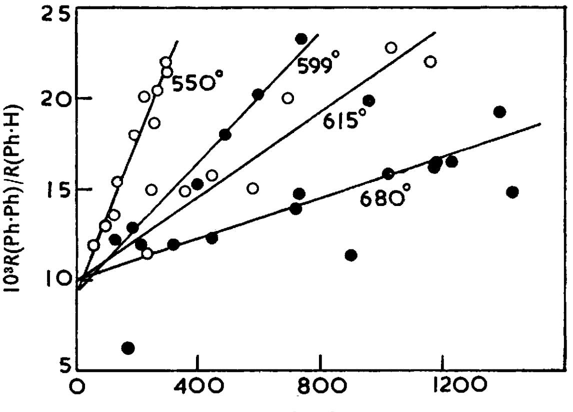

FIG. 1. The photolysis of acetophenone at 550°, 599°, 615°, and 680°K.

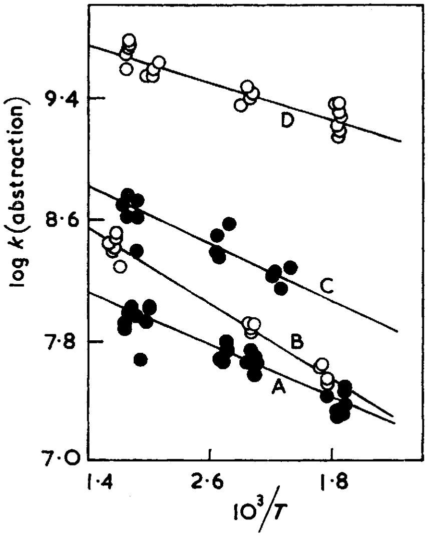

FIG. 2. The reaction of methyl radicals with acetophenone (A) and of phenyl radicals with methane (B), cyclopropane (C), and isobutane (D)

Similar experiments were carried out with cyclopropane and isobutane. It can be seen from Fig. 2 that the results were less reproducible largely because of analytical difficulties. The activation energies and A factors are given in Table 3.

TABLE 3.

The reactions of phenyl and methyl radicals at 333°.

$\mathrm{Ph + RH = PhH + R;\ Me + RH = MeH + R.}$

	Phenyl			Methyl				
RH	log A	E	log k	log A	E	log k	Ref.	log ($k_{\text{Ph}}/k_{\text{Me}}$)
Methane	11·9	11·1	7·9	11·8	14·7	6·5	*a*	1·4
Cyclopropane	11·4	8·5	8·3	11·0	10·3	7·2	*b*	1·1
Isobutane	11·8	6·7	9·4	11·0	7·6	8·3	*b*	1·1
Acetophenone	11·6	6·2	9·4	10·7	7·4	8·0	*c*	1·3

A in mole^{-1} cm.^{3} sec.$^{-1}$; E in kcal. mole^{-1}.

a, Dainton, Ivin, and Wilkinson, *Trans. Faraday Soc.*, 1959, **55**, 929; *b*, Trotman-Dickenson, "Gas Kinetics," Butterworths, London, 1955; *c*, This work.

The strength of the C–H bond in benzene can be found from the activation energy of reaction (8) and of the reverse reaction together with the known value of D(Me–H).[2] The only determination [3] of the activation energy of the reverse reaction (9·2 kcal./mole)

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[2] Fettis and Trotman-Dickenson, *J.*, 1961, 3037.

[3] Trotman-Dickenson and Steacie, *J. Chem. Phys.*, 1951, **19**, 329.

is not particularly reliable, but the activation energy for the attack of trifluoromethyl radicals has been twice determined (7·7 and 6·3 kcal./mole).[4] The second determination appears to be a good one. The relation between the rate constants for the attack of methyl and of trifluoromethyl radicals on benzene is in line with that for attack on other compounds.[5] The value of 9·2 kcal./mole is, therefore, probably not in error by more than one or at most two kcal./mole. We therefore have

$$D(\text{Ph–H}) = 103{\cdot}9 - (11{\cdot}1 - 9{\cdot}2) = 102{\cdot}0 \text{ kcal./mole,}$$

This value is in good agreement with values derived from the pyrolysis of phenyl bromide (101·4 kcal./mole). The present derivation is based on the assumption that a methyl radical reacts by direct hydrogen abstraction and not by preliminary addition as does trifluoromethyl.

Table **3** shows that the reactivities of phenyl radicals with different substrates are parallel to those of methyl radicals. The existence of the parallelism does not depend upon the assumption that has been made that phenyl radicals combine on every collision, but the numerical relation does. If the high rate of combination is accepted then phenyl radicals are slightly less reactive than trifluoromethyl radicals.

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[4] Pritchard, Pritchard, Schiff, and Trotman-Dickenson, *Trans. Faraday Soc.*, 1956, **52**, 849; Charles and Whittle, *ibid.*, 1960, **56**, 794.

[5] Trotman-Dickenson, *Chem. and Ind.*, 1957, 1243.