

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY COLLEGE OF FORESTRY AT SYRACUSE UNIVERSITY, SYRACUSE 10, NEW YORK]

Competitive Abstraction of H and D Atoms by Radicals Formed in the Decomposition of Acetyl Peroxide, *t*-Butyl Peroxide and in the Photolysis of Azomethane¹

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The competitive abstraction by methyl radicals of H and D from partially deuterated ethylbenzene was studied over temperature range 50–143°. Three systems were used for radicals production: *t*-butyl peroxide, acetyl peroxide and photolysis of azomethane. Self-consistent results were obtained which indicate that the observed reactions are due to the same species, namely, a methyl radical. One has to conclude that reactions observed in the acetyl peroxide system are due to methyl radicals and not to acetate radicals which decarboxylate as they react. Significance of the difference of the activation energies of H and D abstractions is discussed.

Addition of methyl radicals to many aromatic, olefinic and acetylenic compounds was studied extensively in this Laboratory.² The radicals were produced by the thermal decomposition of acetyl peroxide, but this mode of generation of methyl radicals raised the question of identity of the reacting species. The problem is this. Are the observed addition reactions caused indeed by the methyl radicals produced by a rapid decarboxylation of the primary acetate radicals, or do they result from reactions of acetate radicals with the investigated substrates, their decarboxylation taking place simultaneously with the investigated addition? It was tentatively suggested that the first alternative is the correct one,³ but a conclusive proof requires reinvestigation of some of the previously studied reactions using, however, a different source for methyl radicals. This was done recently by Steel and Szwarc,⁴ who reinvestigated the addition of methyl radicals to propene and butene-1 in a system in which photolysis of azomethane was the source of the radicals. Their results agreed closely with those of Buckley and Szwarc⁵ who used the decomposition of acetyl peroxide for generation of radicals. Hence, it appears that the attacking radicals formed in the thermal decomposition of acetyl peroxide are indeed methyl radicals.

The only reported evidence contradicting this conclusion is based on the work of Urry.⁶ His claim is based on studies of competitive H and D abstractions from deuterated ethylbenzene (C₆H₅·CHD·CH₃), the abstracting radicals being generated by the thermal decomposition of acetyl peroxide and *t*-butyl peroxide, respectively. The ratio CH₃D/CH₄ was found to be different in both cases and different activation energies were calculated from results obtained with acetyl peroxide and *t*-butyl peroxide. It was decided, therefore, to repeat Urry's experiments and actually three systems generating methyl radicals were used: thermal decomposition of *t*-butyl peroxide, of acetyl peroxide and photolysis of azomethane. The results, re-

ported in this paper, indicate again that the reacting species formed in the decomposition of acetyl peroxide are indeed methyl radicals.

Experimental

Deuterated ethylbenzene was prepared by catalytic hydrogenation of styrene with 99% pure deuterium using Raney nickel.⁷ Unfortunately, ordinary alcohol was used in the preparation and thus some undesirable exchange did take place. Consequently, the final product contained only ~50% of the expected deuterium. The deuterated ethylbenzene was dried over sodium to remove the last trace of alcohol and then distilled. Its chemical purity was checked by gas chromatography and no impurities were detected.

The deuterated ethylbenzene was used in preparing the following solutions: 10⁻¹ and 10⁻² M *t*-butyl peroxide, 10⁻² and 10⁻³ M acetyl peroxide and 5.10⁻³ M azomethane. The usual methods were used in purifying the peroxides. Azomethane was prepared by oxidation of *sym.* dimethylhydrazine⁸ and purified by the standard technique. Its purity was also confirmed by gas-chromatography.

The respective solutions were eventually deaerated in high vacuum (see ref. 4 for details of deaeration of azomethane solution) and then sealed in glass ampules provided with break seals. The peroxide solutions were heated for predetermined periods of time at desired temperatures. The temperature of the thermostatic baths was kept constant within 0.1°. The azomethane solutions were photolyzed at temperatures kept constant within ±1/2° using a General Electric A-H6 mercury arc lamp. The light of the lamp was filtered through a 20 cm. thickness layer of ethylbenzene to avoid excitation of ethylbenzene molecules in the experiment. (Experiments carried out without the light filter were irreproducible and gave higher values for the CH₃D/CH₄ ratio than those listed in Table I. Apparently the difference in the reactivities of the C-H and C-D bonds decreases in the excited ethylbenzene molecule.) Thereafter, the ampules were attached to the analytical apparatus and the products pumped into a calibrated storage flask using a Hg-diffusion pump and Toepler pump working in series. The gases passed through a trap held at -110°, where most of the ethylbenzene condensed and then through two more traps held at -190° where all the other products but CH₃D, CH₄ and (in photolysis experiments) N₂ were condensed. The composition of the non-condensable gases was determined mass-spectrographically.

The mass-spectrometer used in this work was Consolidated Engineering Corp. 103-C instrument. To insure the required instrument reproducibility all the investigated samples were analyzed on the same day. The stability of the mass-spectrometer was 1%, as shown by periodic measurements with pure methane.

The ratio CH₃D/CH₄ was determined by intensities of the 15 and 17 m./e. peaks. (The peak 16 m./e. was used only in the check. Due to trace amounts of O₂ in the sample its reliability was less satisfactory.) Since both compounds contribute to these peaks the quantity of each component was calculated by means of simultaneous equations. The necessary matrix was constructed from the mass patterns of

(1) This work was supported by the Office of Ordnance Research of U. S. Army through Contract Number DA-30-115-ORD-678.

(2) (a) M. Levy and M. Szwarc, *THIS JOURNAL*, **77**, 1949 (1955).

(b) M. Szwarc and J. H. Binks, "Theoretical Organic Chemistry," Kekule Symposium, Butterworth Publ., London, 1959, p. 262.

(3) M. Levy and M. Szwarc, *THIS JOURNAL*, **76**, 5981 (1954).

(4) C. Steel and M. Szwarc, *J. Chem. Phys.*, in press.

(5) R. P. Buckley and M. Szwarc, *Proc. Roy. Soc. (London)*, **A240**, 396 (1957).

(6) W. H. Urry, Paper read at the Organic Symposium, Denver, June, 1950.

(7) E. E. Royals, "Advanced Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1956, p. 97.

(8) R. Renaud and L. C. Leitch, *Can. J. Chem.*, **32**, 545 (1954).

TABLE I

Radical source	Concn., M	Temp., °C.	$\frac{\text{CH}_3\text{D}}{\text{CH}_4} \cdot 10^2$
Azomethane	$5 \cdot 10^{-3}$	50.7	5.24
Azomethane	$5 \cdot 10^{-3}$	50.7	5.15
Acetyl peroxide	$1 \cdot 10^{-2}$	55.1	5.66
Acetyl peroxide	$1 \cdot 10^{-2}$	55.1	5.61
Acetyl peroxide	$1 \cdot 10^{-3}$	55.1	5.82
Azomethane	$5 \cdot 10^{-3}$	60.1	5.49
Azomethane	$5 \cdot 10^{-3}$	60.1	5.47
Acetyl peroxide	$1 \cdot 10^{-2}$	65.2	6.24
Acetyl peroxide	$1 \cdot 10^{-2}$	65.2	6.12
Acetyl peroxide	$1 \cdot 10^{-3}$	65.2	5.91
Azomethane	$5 \cdot 10^{-3}$	69.6	5.85
Azomethane	$5 \cdot 10^{-3}$	69.6	5.82
Acetyl peroxide	$1 \cdot 10^{-2}$	75.8	6.37
Acetyl peroxide	$1 \cdot 10^{-2}$	75.8	6.46
Acetyl peroxide	$1 \cdot 10^{-3}$	75.8	6.37
Azomethane	$5 \cdot 10^{-3}$	79.5	6.15
Azomethane	$5 \cdot 10^{-3}$	79.5	6.16
Acetyl peroxide	$1 \cdot 10^{-2}$	85.1	6.78
Acetyl peroxide	$1 \cdot 10^{-2}$	85.1	6.73
Acetyl peroxide	$1 \cdot 10^{-3}$	85.1	6.99
<i>t</i> -Butyl peroxide	$1 \cdot 10^{-1}$	99.7	7.31
<i>t</i> -Butyl peroxide	$1 \cdot 10^{-2}$	99.7	7.33
<i>t</i> -Butyl peroxide	$1 \cdot 10^{-1}$	111.1	7.53
<i>t</i> -Butyl peroxide	$1 \cdot 10^{-2}$	111.1	7.75
<i>t</i> -Butyl peroxide	$1 \cdot 10^{-1}$	125.9	8.30
<i>t</i> -Butyl peroxide	$1 \cdot 10^{-1}$	134.0	8.70
<i>t</i> -Butyl peroxide	$1 \cdot 10^{-2}$	134.0	8.60
<i>t</i> -Butyl peroxide	$1 \cdot 10^{-1}$	143.2	9.15
<i>t</i> -Butyl peroxide	$1 \cdot 10^{-2}$	143.2	9.28

pure components. The mass-spectrum of CH_3D was constructed from the directly observed mass-spectrum of pure methane by using the method of Schissler, Thompson and Turkevich.⁹ The necessary weighting factors *a* and *b* were taken, however, from the publication by Dibeler and Mohler,¹⁰ since these workers employed a 180° sector type mass-spectrometer similar to that used in this investigation. The validity of these calculations was confirmed by agreement within 1% between the calculated and the observed intensity of the 16 m./e. peak.

Results

The results of this investigation are given in Table I and in Fig. 1. It is particularly gratifying to notice the constancy of the $\text{CH}_3\text{D}/\text{CH}_4$ ratio on a 10 fold change in the concentration of acetyl peroxide and *t*-butyl peroxide. The actual differences in these ratios are small and well within experimental errors. The inspection of the data shows that the same species is involved in all these reactions, and hence in each case the methyl radical must be responsible for the observed abstraction.

A closer inspection of the data shows, however, a small difference in the $\text{CH}_3\text{D}/\text{CH}_4$ ratio depending on whether acetyl peroxide or azomethane is used in generating the radicals. The $\text{CH}_3\text{D}/\text{CH}_4$ ratio is higher by 5% in the former system, and this small difference cannot be attributed to the different abundance of C^{13} in these compounds. Indeed, even if the relative abundance of C^{13} in these two compounds would differ by 10% this would lead to a change in the $\text{CH}_3\text{D}/\text{CH}_4$ ratio of 1% only.

(9) D. O. Schissler, S. O. Thompson and V. Turkevich, *Discussions Faraday Soc.*, **10**, 46 (1951).

(10) V. H. Dibeler and F. L. Mohler, *J. Research Natl. Bur. Standards*, **45**, 441 (1950).

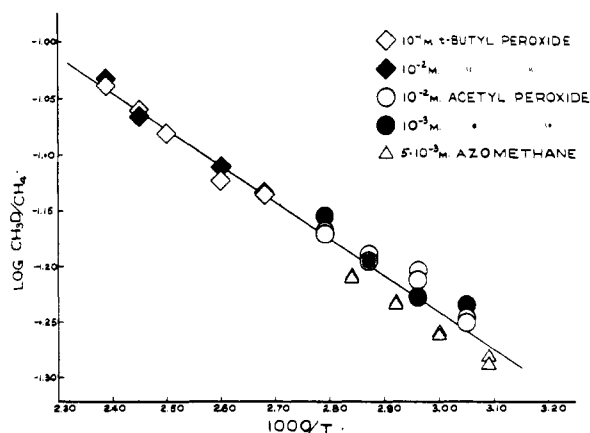
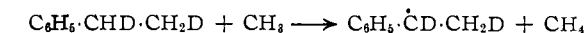
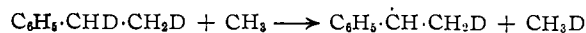


Fig. 1.

One has to consider now the possible "hot" radical reactions. Both the photolysis of azomethane and the thermal decomposition of acetyl peroxide might produce hot radicals (the decarboxylation of CH_3COO radicals is exothermic to an extent of 17 kcal./mole¹¹ and a part of this energy might appear in the methyl radicals). On the other hand, no "hot" methyl radicals can possibly be formed by the decomposition of *t*-butyl peroxide. The extrapolation of the results obtained in the *t*-butyl peroxide system agrees so well with those observed in the acetyl peroxide system that the possibility of "hot" radical reaction seems to be very remote. Nevertheless, one may calculate what should be the fraction of "hot" methyl radicals in the abstraction reaction to account for the 5% difference in the $\text{CH}_3\text{D}/\text{CH}_4$ ratios which was observed in the acetyl peroxide and azomethane systems. The difference in activation energies of D and H abstractions is determined as 1.6 kcal./mole (see Fig. 1). It is plausible to expect no difference in activation energies of the D and H abstractions if they are due to "hot" methyl radicals, and this means that the $\text{CH}_3\text{D}/\text{CH}_4$ ratio in such a reaction should be about 10 times greater than that observed in a normal reaction. Therefore, presence of 0.5% of "hot" radicals would account for the observed 5% difference in the $\text{CH}_3\text{D}/\text{CH}_4$ ratio. We believe that even this value is too high and that the observed difference is most probably due to some instrumental factors. (Work of J. R. McNesby and A. S. Gordon, *THIS JOURNAL*, **76**, 4196 (1954) demonstrates absence of "hot" methyl radicals in the photolysis of acetone. Abstraction of a hydrogen from azomethane does decrease the observed $\text{CH}_3\text{D}/\text{CH}_4$ ratio. However, in view of the low concentration of azomethane it is improbable that this reaction would account for more than 0.1% of CH_4 formed.)

Activation Energies of H and D Abstraction.—Using the least square method we calculated the difference ΔE in activation energies of the reactions



to be 1.56 ± 0.1 kcal./mole. Very similar results were obtained in reactions involving other com-

(11) I. Jaffe, E. J. Prosen and M. Szwarc, *J. Chem. Phys.*, **27**, 416 (1957).

TABLE II

Investigated system	$\Delta E,^a$ kcal./mole	Reference
$H_2 + CH_3 \rightarrow H + CH_3$	1.8	Photolysis, ^b 134-290°
$D_2 + CH_3 \rightarrow D + CH_3D$		
$CH_3CO \cdot CH_3 + CH_3 \rightarrow$ $CH_3CO \cdot CH_2 + CH_4$	1.64	Photolysis, ^c 150-250°
$CD_3COCD_3 + CH_3 \rightarrow$ $CD_3CO \cdot CD_2 + CH_3D$		
$CH_3 \cdot CO \cdot CH_3 + CH_3 \rightarrow$ $CH_3 \cdot CO \cdot CH_2 + CH_4$		
$CD_3CO \cdot CD_3 + CH_3 \rightarrow$ $CD_3CO \cdot CD_2 + CH_3D$		
$CH_3 \cdot CHO + CH_3 \rightarrow$ $CH_3 \cdot CO + CH_4$	1.67	Pyrolysis, ^d 466-525°
$CH_3 \cdot CDO + CH_3 \rightarrow$ $CH_3 \cdot CO + CH_3D$		
	1.1	Photolysis, ^e 27-165°

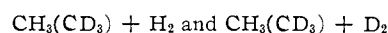
^a It is assumed that CH_3 and CD_3 radicals react with the same activation energy. ^b E. Whittle and E. W. R. Steacie, *J. Chem. Phys.*, **21**, 993 (1953); see also J. R. McNesby, A. S. Gordon and S. R. Smith, *THIS JOURNAL*, **78**, 1287 (1956). ^c J. R. McNesby and A. S. Gordon, *ibid.*, **76**, 1416 (1954). ^d J. R. McNesby, T. W. Davis and A. S. Gordon, *ibid.*, **76**, 823 (1954). ^e P. Ausloos and E. W. R. Steacie, *Can. J. Chem.*, **33**, 31 (1955).

pounds and the best set of data is collected in Table II. It is necessary to state, however, that a few more systems were investigated, the results leading to ΔE 's different from those quoted in Table II, e.g., $CH_3 + CH:CH$ or $CD:CD$, $\Delta E = 4.4$ kcal./mole,¹² or $CH_3 + C_2H_6$ and C_2D_6 giving $\Delta E = 3.3$ kcal./mole.¹³ It seems, however, that some unknown factors complicate these reactions and this vitiates the ΔE values. (In a letter to one of us Dr. Gordon expressed his doubts in the ΔE value obtained for the system $C_2H_6-C_2D_6$, although he is unable to spot any error in his experimental results.) Indeed, the work of Steacie and his school shows clearly the difficulty of accurate determination of ΔE , e.g., their earlier results¹⁴ obtained for the system

(12) C. H. Drew and A. S. Gordon, *J. Chem. Phys.*, **31**, 1417 (1959).

(13) J. R. McNesby and A. S. Gordon, *THIS JOURNAL*, **77**, 4719 (1955).

(14) T. G. Majury and E. W. R. Steacie, *Discussions Faraday Soc.*, **14**, 45 (1953).



lead to ΔE values varying from 0.7 to 2.5 kcal./mole.

Our present results, as well as those quoted in Table II, show that ΔE is equal to the difference in the respective zero-point energies. For example, difference in zero-point energies of H_2 and D_2 amounts to 1.8 kcal./mole, and ΔE is also 1.8 kcal./mole, difference in C-H and C-D zero-point energies is 1.25 kcal./mole (from infrared spectra) the observed ΔE vary from 1.1 to 1.6 kcal./mole. This fact was recognized clearly by Bigeleisen¹⁵—it indicates the same configuration for the transition states in H and D abstractions and no zero-point energy in the transition state.

We prepared recently a sample of $C_6H_5CHDCH_3$ by reducing α -chloroethylbenzene with $LiD + LiAlD_4$ using the procedure described by Eliel.¹⁶ Mass-spectroscopic analysis showed that the final product contained 96% of the required deuterated compound and 4% of ordinary ethylbenzene. Using this sample we determined ν_D/ν_H , i.e., the ratio of the respective frequency factors of D or H abstraction reactions. The ratio CH_3D/CH_4 was determined at 132.3° using decomposition of di-*t*-butyl peroxide and at 49.1° using photolysis¹ of azo-methane. On the basis of previously determined $\Delta E = E_D - E_H$, we obtained for ν_D/ν_H values 1.28 and 1.24, respectively. It is interesting to note that ν_D/ν_H determined by McNesby and Gordon for reactions $CH_3 + CH_3COCH_3$ and $CH_3 + CD_3CO \cdot CD_3$ are 1.18 (ref. *c* of Table II) and 1.28 (ref. *d* of Table II). The agreement with our results seems to be well within experimental errors of these determinations.

While the present results were obtained in a liquid phase, those quoted in Table II arise from the work carried out in the gas phase. The agreement between these results indicates, therefore, that the course of a bimolecular free radicals reaction in a nonpolar solvent resembles closely that in the gas phase.

(15) J. Bigeleisen, *J. Chem. Phys.*, **17**, 675 (1949).

(16) E. L. Eliel, *THIS JOURNAL*, **71**, 3970 (1947).

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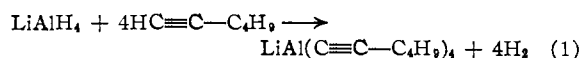
Lithium Aluminum Amides as Catalysts for the Reaction of Lithium Aluminum Hydride with 1-Hexyne¹

By GEORGE B. SMITH, DARL H. MCDANIEL, EDWARD BIEHL AND C. A. HOLLINGSWORTH

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The rate of reaction of lithium aluminum hydride with 1-hexyne in ether has been studied. Catalysts for this reaction have been produced by the reaction of excess lithium aluminum hydride in ether on amines and related compounds.

By measuring the hydrogen evolved we have studied the rate of reaction of lithium aluminum hydride with 1-hexyne in ethyl ether at temperatures from 35 to 42°. The total hydrogen evolved is consistent with



(1) This work was sponsored by the Office of Ordnance Research, U. S. Army.

and there is no evidence of reduction of the triple bond, in agreement with results reported² for the reaction in dioxane. However, in a mixture of *n*-butyl ether and ethyl ether at 90°, less than the theoretical amount of hydrogen was evolved, and the infrared spectrum indicates that some alkyne was reduced to alkene.

(2) W. J. Bailey and C. R. Pfeifer, *J. Org. Chem.*, **20**, 1337 (1955).