[Contribution from the Chemistry Department, New York State College of Forestry at Syracuse University]

n-Propyl Affinities of Aromatic and Olefinic Compounds

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Relative rates of addition of *n*-propyl radicals to aromatic and olefinic compounds were determined. The propyl radicals were generated by the thermal decomposition of butyryl peroxide. It was shown that the log-log plots of propyl affinity *versus* methyl or ethyl affinities result in straight lines with a slope of unity. These results are interpreted as an indication that the intrinsic reactivities for an addition reaction are identical for *n*-propyl, ethyl and methyl radicals. Further inspection of the data seems to indicate that ethyl and propyl radicals are similar in their efficiency to abstract an hydrogen atom from the solvent, and the latter observation seems to point out that $D(C_2H_5{-}H) \approx D(n\text{-}C_3H_7{-}H)$.

Previous studies of the addition of methyl[1] and ethyl[2] radicals to aromatic or olefinic compounds led to the concept of intrinsic reactivity of radicals. It was found that linear relations correlate the logarithms of rate constants of addition of various radicals to the same series of aromatic or olefinic compounds. Hence, denoting by k_i and k_j the rate constants of reactions

$$CH_3 + A_i \longrightarrow CH_3{\cdot}A_i \qquad (k_i)$$

$$CH_3 + A_j \longrightarrow CH_3{\cdot}A_j \qquad (k_j)$$

and by k'_i and k'_j the corresponding rate constants of addition reactions involving another radical R, one finds that

$$\log (k'_i/k'_j) = \alpha \log (k_i/k_j)$$

where α is independent of the choice of the compounds A_i or A_j.[3] It appears that such a linear relation results from a following relation between the respective activation energies

$$E'_i - E'_j = \alpha(E_i - E_j)$$

and that α (*i.e.*, the slope of the straight line obtained from the log-log plot) measures the reactivity of radical R as compared to the reactivity of methyl radical. It has been proposed to refer to α as the intrinsic reactivity of a radical, and one notices that α plays a role similar to ρ in Hammett's σ,ρ relation.

These values of α already have been obtained in previous studies: α for CCl_3 radical = 1.9[1]; α for C_2H_5 radical = 1.0[2]; α for styryl radical = 2.2.[4] We believe that the determination of α for a series of radicals should deepen our knowledge of quantitative radical chemistry. This paper is concerned with the determination of the intrinsic reactivity of the *n*-propyl radical.

This determination requires a thorough study of reactions described by the general equation

$$n\text{-}C_3H_7 + A \longrightarrow n\text{-}C_3H_7A$$

The propyl radicals were generated by the thermal decomposition of *n*-butyryl peroxide. Kinetics of this decomposition, followed by the disappearance of the peroxide, was reported in an earlier communication.[5] It was found that the reaction follows first-order kinetics at low concentration of the peroxide, and the results were interpreted in terms of a unimolecular decomposition

$$C_3H_7{\cdot}CO{\cdot}O{\cdot}O{\cdot}CO{\cdot}C_3H_7 \longrightarrow 2C_3H_7{\cdot}COO{\cdot}$$

Thermochemical studies of Jaffe, Prosen and Szwarc[6] indicate that the dissociation of C_3H_7COO radical into $n\text{-}C_3H_7$ radical and carbon dioxide is *exothermic* to an extent of about 12 kcal./mole, and hence it is highly probable that the C_3H_7COO radicals decompose as soon as they are formed yielding *n*-propyl radicals. We examined the products of the decomposition of butyryl peroxide in isoöctane solution and found C_3 hydrocarbons and carbon dioxide as the products of the reaction.[7] The quantitative results of these analyses are given in Table I, inspection of which shows that the first-order rate constant k_u, measured by the amount of carbon dioxide formed, agrees well with the constant computed on the basis of peroxide decomposed.[5] The slight increase in these rate constants with increasing concentration of the peroxide indicates some interference due to induced decomposition (see in this connection ref. 5).

The ratio of C_3 hydrocarbons to carbon dioxide is essentially constant. The only considerable deviation is observed in a more concentrated solution at 85°. It seems that propyl radicals formed in the decomposition of the peroxide react sufficiently rapidly with the solvent giving propane

$$n\text{-}C_3H_7 + \text{isoöctane} \longrightarrow C_3H_8 + \text{isoöctyl radical} \quad (1)$$

Consequently, their stationary concentration is sufficiently low to prevent a bimolecular recombination or an interaction with the solvent radicals formed in reaction 1. Hence, the amount of propane formed measures essentially the number of propyl radicals which escaped from the "cage" and are available for reaction 1. However, if the stationary concentration of radicals is high a bimolecular reaction involving two radicals is more and more important and then the ratio (C_3 hydrocarbons)/CO_2 decreases. Such a trend is observed when we compare the second and third line of Table I (the result of increasing concentration of the peroxide by factor of ten) and it is even more pronounced when we compare the last two lines of Table I. In these experiments, carried out at 85°, the decomposition proceeds about 15 times

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[1] M. Szwarc, *J. Polymer Sci.*, **16**, 367 (1955); M. Levy and M. Szwarc, This Journal, **77**, 1949 (1955).

[2] J. Smid and M. Szwarc, *ibid.*, **78**, 3322 (1956).

[3] A_i and A_j denote aromatic or olefinic molecules to which the radicals add.

[4] A. Rembaum and M. Szwarc, This Journal, **77**, 4468 (1955).

[5] J. Smid, A. Rembaum and M. Szwarc, *ibid.*, **78**, 3315 (1956).

[6] The results of these studies are in the course of publication. See also ref. 2 and 5.

[7] Study of this decomposition proceeding in the gas phase by A. Rembaum and M. Szwarc, *J. Chem. Phys.*, **23**, 909 (1955), demonstrated that *n*-hexane is also a product of the reaction. However, technical difficulties prevented us from isolating this product from our system.

TABLE I

DECOMPOSITION OF BUTYRYL PEROXIDE IN ISOÖCTANE

Temp., °C.	Time, (hr.)	Concn. of peroxide $\times 10^2$, *M*	No. of expt.	$\frac{C_3 \text{ hyd.}}{CO_2}$	$k_u \times 10^5$, sec.$^{-1}$ (CO$_2$)	$k_u \times 10^5$, sec.$^{-1}$ (Peroxide)[a]
55	8	1.37	3	0.577 ± 0.001	0.235	...
65	20	0.137	3	.580 ± .002	0.93	0.91
65	2	1.37	12	.546 ± .003	1.08	1.16
85	1.50	0.136	3	.563 ± .006	15.4	13.5
85	1.25	1.37	3	.380 ± .004	16.7	16.2

[a] These values are interpolated from the data reported in ref. 5.

faster than in experiments carried out at 65°, and therefore the stationary concentration of radicals is considerably higher than in the other experiments.

Further studies indicate that a small fraction of the C_3 hydrocarbons formed in the decomposition results from a cage disproportionation. This is shown by the data presented in Table II which lists the results of experiments carried out in presence of quinone. The latter compound acts as an efficient scavenger of free radicals and thus prevents the occurrence of reaction 1 since it removes rapidly the *n*-propyl radicals formed in the decomposition. The data collected in Table II show clearly that a constant amount of C_3 hydrocarbons is formed in the reaction independently of the concentration of quinone. This result is interpreted as an indication that two propyl radicals formed from *the same* molecule of butyryl peroxide have a finite probability to interact and disproportionate. The probability of such a "cage" disproportionation is only slightly affected by the concentration of the quinone (if the latter is not too high). A similar phenomenon was observed in the decomposition of propionyl peroxide (see ref. 5), and it is interesting to notice that the ratio (residual C_2 hydrocarbons)/CO_2 observed in the decomposition of propionyl peroxide is the same as the ratio (residual C_3 hydrocarbons)/CO_2 observed in the present study, namely, 0.077.

TABLE II

DECOMPOSITION OF BUTYRYL PEROXIDE IN PRESENCE OF QUINONE

All experiments carried out at 65° and in 1.37 10^{-2} *M* solution

Concn. of benzoquinone, mole %	$\frac{\text{Residual } C_3}{CO_2}$	$k_u \times 10^5$, sec.$^{-1}$
0	0.546	1.08
0.05	.075	0.99
.1	.076	1.00
.15	.079	0.98
.25	.079	.97
Av.	.077	..

The decomposition carried out in a solution containing an aromatic or olefinic compound in addition to isoöctane produces less C_3 hydrocarbons than the reaction carried out under identical conditions but in absence of an aromatic or olefinic compound. The decrease in the amount of C_3 hydrocarbons formed is explained on the assumption that reaction 2 competes with reaction 1 for

$$n\text{-}C_3H_7 + A \longrightarrow n\text{-}C_3H_7\cdot A \qquad (2)$$

propyl radicals. Accepting the premises, clearly stated and subsequently justified in ref. 1 and 2, we calculate the ratio k_2/k_1 from the equation

$$k_2/k_1 = \frac{(C_3H_8 \text{ "lost" in presence of A})}{(C_3H_8 \text{ formed in presence of A})} \times \frac{X_{HS}}{X_A}$$

In this equation X_{HS} and X_A denote the mole fractions of solvent and the compound A in the reacting mixture, the expression (C_3H_8 formed in presence of A) denotes the amount of propyl radicals reacted according to eq. 1, while the expression (C_3H_8 "lost" in presence of A) denotes the amount of propyl radicals reacted according to eq. 2. This equation can be converted into the expression

$$\frac{k_2}{k_1} = \frac{(C_3H_8/CO_2)_{\text{in absence A}} - (C_3H_8/CO_2)_{\text{in presence A}}}{(C_3H_8/CO_2)_{\text{in presence A}}} \times \frac{X_{HS}}{X_A}$$

The experimental data provide us with the ratios (C_3 hydrocarbons)/CO_2, and in order to use them in the calculation of k_2/k_1 we have to subtract the constant ratio (residual C_3/CO_2) from the fraction (C_3 formed in absence of A)/CO_2. This correction does not apply to the numerator since subtraction of (residual C_3)/CO_2 cancels in the calculations (see also ref. 2).

TABLE III

ALL EXPERIMENTS CARRIED OUT AT 65°

Compound A	Concn., mole %	$\frac{C_3 \text{ hyd.}}{CO_2}$	k_2/k_1	$k_u(CO_2) \times 10^5$, sec.$^{-1}$
Benzene	5	0.506	1.77	1.15
Benzene	15	.433	1.79	1.26
Benzene	30	.356	1.59	1.35
Benzene	45	.288	1.43	1.40
Benzene	60	.238	1.27	1.57
Biphenyl	2	0.460	11.0	1.15
Biphenyl	4	.426	8.3	1.12
Biphenyl	6	.385	8.2	1.18
Biphenyl	10	.327	7.9	1.22
Naphthalene	0.5	0.422	72	1.04
Naphthalene	1.0	.363	64	1.03
Naphthalene	2.0	.277	65	1.02
Naphthlene	3.0	.223	71	0.97
Phenanthrene	0.4	0.427	85	1.08
Phenanthrene	0.8	.346	92	1.10
Phenanthrene	1.2	.294	96	1.14
Phenanthrene	2.0	.248	85	1.13
Stilbene (*trans*)	0.1	0.312	995	1.09
Stilbene (*trans*)	.2	.248	870	1.06
Stilbene (*trans*)	.3	.201	935	1.06
Stilbene (*trans*)	.4	.169	815	1.07
Benzophenone	1.0	0.423	35	1.12
Benzophenone	2.0	.363	31	1.11
Benzophenone	3.0	.303	35	1.18
Benzophenone	5.0	.251	32	1.21
Quinoline	0.52	0.343	146	1.21
Quinoline	1.0	.263	150	1.26
Quinoline	1.5	.225	142	1.28
Vinyl acetate	0.2	0.394	245	1.10
Vinyl acetate	.3	.346	247	1.08
Vinyl acetate	.6	.268	242	1.09
Vinyl acetate	1.0	.214	240	1.09

All the experimental data are given in Table III. The third column of this table gives the (C_3/CO_2) actually found in each experiment. The value (C_3/CO_2) formed in absence of A is taken from Table I, and since all the experiments were carried out at 65° with concentration of peroxide $1.37 . 10^{-2}$ *M* the respective value 0.546 ± 0.003 is chosen. Finally, the value of (residual C_3/CO_2) is taken from Table II.

The following points need emphasis. Variation in the concentration of compound A by a factor as high as 5 or 6 leads to a negligible variation in the calculated value of k_2/k_1. (Benzene is the only outstanding exception. We believe that the reasons for such a behavior, discussed in reference 2, are applicable to the present situation, and that the correct value of k_2/k_1 for benzene is obtained by extrapolating the experimental results to zero concentration of benzene.) The presence of compound A does not affect the rate of the unimolecular decomposition of the peroxide as shown by the data listed in the last column of Table III. The small deviations observed in the case of benzene and quinoline are understandable and the reasons are discussed in ref. 1. Hence, we believe that our measurements yield indeed the required k_2/k_1, which we will refer to as the relative propyl affinities. The average values of k_2/k_1 for *n*-propyl radicals are listed in Table IV. In addition we listed there the *n*-propyl affinities calculated in a scale in which propyl affinity of benzene is unity. For the sake of comparison we included in Table IV the k_2/k_1 values for ethyl radicals as well as the values for ethyl and methyl affinities.

The plot of log *n*-propyl affinities *versus* log methyl affinities and a similar plot involving propyl and ethyl affinities are shown in Figs. 1 and 2. In both cases the slopes are unity, indicating that intrinsic reactivities of methyl, ethyl and *n*-propyl radicals are the same. It is interesting to notice that the k_2/k_1 values are essentially identical for ethyl and *n*-propyl radicals. This should mean that ethyl and *n*-propyl radicals add to compound A as well as abstract an hydrogen atom from the solvent with an equal ease.[8] Since the driving force for the hydrogen atom abstraction reaction depends on the strength of the R–H bond formed by the radical R, we interpret these results as an indication that $D(C_2H_5\text{–}H) \approx D(C_3H_7\text{–}H)$, and that both dissociation energies are less than $D(CH_3\text{–}H)$. We believe that this conclusion about the strength of C_2H_5–H and *n*-C_3H_7–H bonds are reasonable; however, see in this connection reference 9.

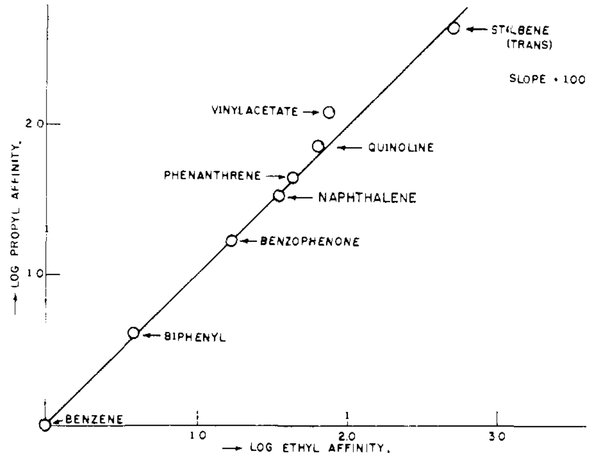

Fig. 1.—Ethyl affinities *vs.* propyl affinities at 65°.

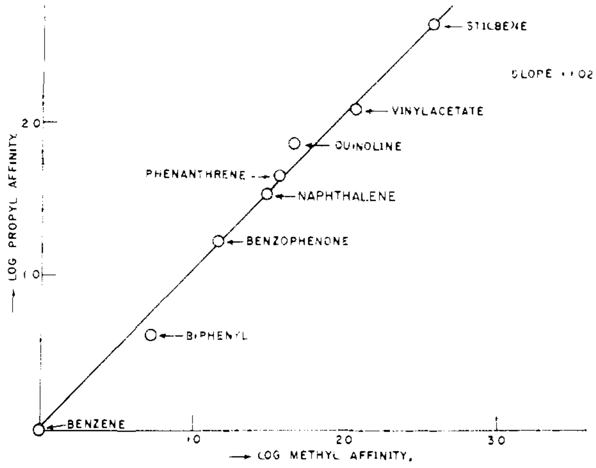

Fig. 2.—Propyl affinities *vs.* methyl affinities at 65°.

Two compounds, namely, vinyl acetate and diphenyl seem to deviate somehow from the linear log-log relation. We repeated the determination of methyl and ethyl affinities of these compounds and found that our present results agree with those reported earlier.[1,2] The significance and the reason of these deviations remain obscure.

Table IV

Compound A	Propyl affinities k_2/k_1	Propyl affinities Bz = 1	Ethyl affinities k_2/k_1	Ethyl affinities Bz = 1	Methyl affinities k_2/k_1	Methyl affinities Bz = 1
Benzene	2.0	(1)	2.9	(1)	0.29	(1)
Biphenyl	8.1 ± 0.2	4.0	11.0	3.8	1.5	5.2
Benzophenone	33.5 ± 1.6	16.8	50	17.0	4.2	14.5
Naphthalene	68.3 ± 3.6	34.2	100	34.5	8.7	30
Phenanthrene	90 ± 4	45	124	43	10.7	37
Quinoline	146 ± 3	73	182	63	13.4	46
Vinyl acetate	244 ± 3	122	214	74	37	128
Stilbene (*trans*)	900 ± 60	450	1440	496	109	376

Experimental

Deaerated solutions of butyryl peroxide in isoöctane containing the required amount of the investigated aromatic or olefinic compound were sealed off in a glass ampoule. The latter were heated for 2 hours at 65°. Thereafter, their contents were analyzed using the apparatus and the technique described earlier.[2,5]

Negligible amounts of permanent gases were found, proving that no methane is formed in the reaction.[10] Distillation from the Ward still showed the presence of C_3 fraction, boiling at the −42 to −47° range. These gases and carbon dioxide were the only gaseous products of the reaction. Their total amount was determined manometrically and their composition by absorbing carbon dioxide on ascarite.

The blank experiments were carried out in identical manner, but the ampoules did not contain any aromatic or olefinic compounds. In the experiments carried out in the presence of quinone, it was shown by the hydrogenation

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(8) This statement needs some reservation. If different steric factors appear in the addition of ethyl and *n*-propyl radicals then the same respective steric factors should appear in the corresponding hydrogen atom abstraction reaction.

(9) C. H. Leigh and M. Szwarc, *J. Chem. Phys.*, **20**, 407 (1952).

(10) Thermal decomposition of propyl radicals yields CH_3 and ethylene. Such a reaction is observed at high temperatures, *i.e.*, above 500°; however, this reaction is immeasurably slow at temperatures below 200°. For further discussion of this point see A. Rembaum and M. Szwarc, *ibid.*, **23**, 909 (1955).

technique that the C_3 fraction contained propylene as well as propane. No attempt was made to isolate hexane.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER]

The Photoöxidation of Diethyl Ketone[1]

BY J. ERIC JOLLEY[2]

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The photochemical reaction between diethyl ketone and oxygen has been studied at temperatures from 35 to 150° at several oxygen pressures and over a wide range of intensities. At all temperatures the carbon monoxide yield becomes small at high oxygen pressures, thus indicating that the propionyl radical reacts with oxygen without producing carbon monoxide. All yields pass through maxima (except possibly carbon monoxide at 35°), and oxygen acts as an inhibitor at high oxygen pressures. At room temperature quantum yields are independent of intensity, but at 150° they are an inverse linear function of the square root of the intensity. Oxygen at very low pressures strongly suppresses the formation of C_2 hydrocarbons so that the reaction between ethyl radicals and oxygen must be very rapid. A fairly complete mechanism for the reaction can be suggested and the relative values of several rate constants estimated. Chains must be propagated mainly by ethoxy and pentanonyl radicals. Since rates of formation of acetaldehyde and carbon dioxide are closely parallel to each other, possibly pentanonyl radicals react with oxygen to give acetaldehyde, carbon dioxide and ethyl radicals.

Introduction

The photolysis of diethyl ketone has been studied, and a mechanism which satisfactorily accounts for the experimental observations has been put forward.[3–6] Information about some of the reactions of radicals with oxygen was obtained[7] in an investigation of the photolysis of mixtures of diethyl ketone and oxygen. The reaction was shown to be a complex radical chain of short length, and various possible radical reactions were discussed. The primary process is almost certainly reaction 1, and it is known that the propionyl radical dissociates almost completely even at room temperature (reaction 2) in the absence of foreign substances. In the presence of oxygen the low yield of carbon monoxide indicates that reaction 2 is largely suppressed. Reaction 3 has been suggested for the reaction of propionyl radicals with oxygen.[7,8]

The present paper gives further data on the diethyl ketone–oxygen reaction. In general, oxygen suppresses formation of C_2 hydrocarbons more completely than hitherto indicated. Due to the chain character of the reaction, great care must be exercised to avoid local depletion of oxygen when the oxygen pressure is low. The higher values for C_2 formation previously reported[7] are thought to be due to such local depletion of oxygen.

Experimental

The reaction was carried out in a high vacuum system consisting essentially of a reaction cell, fractionation spiral, McLeod gage and oxidizing furnace. The parallel light beam entirely filled the cell, and homogeneous conditions were maintained by means of a magnetically driven stirrer. The volume of the part of the line which included the McLeod gage was 663.6 ml., the volume of the reaction system (including stirrer) was 198.8 ml., and the volume of the reaction cell was 76.0 ml.

Two light sources were used (1) a Hanovia Alpine Burner and (2) a water-cooled General Electric Co. A-H6 arc. The beam was collimated by a quartz lens, and radiation below 2300 Å. was removed by a Corning 9863 red-purple Corex filter. Since the long wave absorption limit in diethyl ketone is about 3200 Å., the chief absorbed wave lengths were 3130, 2650 and 2537 Å. Some experiments used a chlorine gas filter so that the main transmitted radiation was 2650 Å. Another series was carried out with a 2-mm. Pyrex plate to give mainly 3130 Å. Intensity effects were studied by neutral density filters of two types—silver coated quartz plates and darkened copper screens. Transmissions were determined by a photo cell and also by a Beckman photometer.

The measurement of the radioactivity of the C^{14}-labeled products was made by freezing them into a proportional counter tube of the type described by Bernstein and Ballantine[9] and counting on a scaler. It was found that the activities of portions of a given sample were directly proportional to their pressures.

Procedure.—A small sample of diethyl ketone, prepared as previously described[5] was removed from the black storage bulb and degassed before being admitted to the cell at 35 mm. pressure, at which pressure all runs were carried out. The desired amount of oxygen (prepared by heating potassium permanganate) was added and the well-stirred mixture illuminated. The gases not condensed by liquid nitrogen (oxygen and carbon monoxide) were removed, measured and transferred to a bulb containing copper–copper oxide which could be heated in a furnace. The resultant carbon dioxide enabled oxygen and carbon monoxide to be calculated. At −160° a second sample, carbon dioxide, was removed and measured, and a third fraction was obtained at −115°. The third fraction was acetaldehyde and was readily characterized by freezing it from the system and causing it to react with *p*-hydroxydiphenyl with which it gives a colored compound with a characteristic absorption peak at 5700 Å.[10]

In experiments at low oxygen pressure, oxygen was added by a "doser" to keep the oxygen pressure approximately constant.[11] Small amounts of ethane and ethylene are produced under these conditions. In these experiments, the non-condensable gases were passed through a fractionation spiral maintained at −215° with supercooled liquid nitrogen. This prevents removal of ethane and ethylene

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[2] Postdoctoral Fellow 1953–1955 under a grant from the Camille and Henry Dreyfus Foundation, Inc.

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