Tetrahedron, 1966, Vol. 22, pp. 509 to 513. Pergamon Press Ltd. Printed in Northern Ireland

AUTOXIDATION OF ISOPROPYL COMPOUNDS—III*

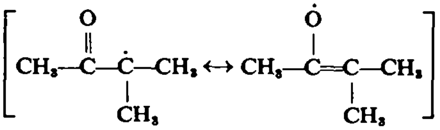
SUBSTITUENT EFFECT ON REACTION RATES

K. Itoh, S. Sakai and Y. Ishii
Department of Synthetic Chemistry, Faculty of Engineering,
Nagoya University, Furo-cho, Chikusa-ku, Nagoya, Japan

(*Received* 18 *May* 1965; *in revised form* 15 *July* 1965)

Abstract—Several isopropyl compounds were autoxidized at 140°. The rates of autoxidation have been correlated linearly with the alpha carbon stabilization energies of the corresponding vinyl monomers. This shows that the stability of the radical formed by hydrogen abstraction plays an important role in the autoxidation of isopropyl compounds.

In preceding papers,[1] it was reported that isopropyl methyl ketone is autoxidized more readily than methyl isobutyrate. The composition of the oxidation products of both these compounds suggests that the tertiary hydrogen atom is attacked exclusively in the primary step of autoxidation. In the case of isopropyl methyl ketone, the stable conjugated radical (I) would be formed.[2]



$$\left[CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-\underset{\underset{\displaystyle CH_3}{|}}{\dot{C}}-CH_3 \leftrightarrow CH_3-\overset{\overset{\displaystyle \dot{O}}{|}}{C}=\underset{\underset{\displaystyle CH_3}{|}}{C}-CH_3 \right]$$

I

As the cross conjugation effect of a methoxy group may be present in methyl isobutyrate, the radical formed by hydrogen abstraction was considered to be stabilized to a lesser extent by the carbonyl group than the corresponding radical from isopropyl methyl ketone.

In this paper, the effect of the conjugation stabilizing ability of the substituents on the autoxidation rates were studied for various isopropyl compounds.

Alfrey and Price[3] proposed the Q–e scheme for the radical polymerization of a number of vinyl monomers and the conjugative contribution of monomers were defined as Q and polymer radicals as P. Recently, Kawabata *et al.*[4] revised the Q values by assuming Q value of styrene as unity. The parameters they proposed seemed to be reasonable, since linear relationship with conjugation stabilization energy was obtained.

---

* Part II, *J. Chem. Soc. Japan*, Industrial Section, to be published.

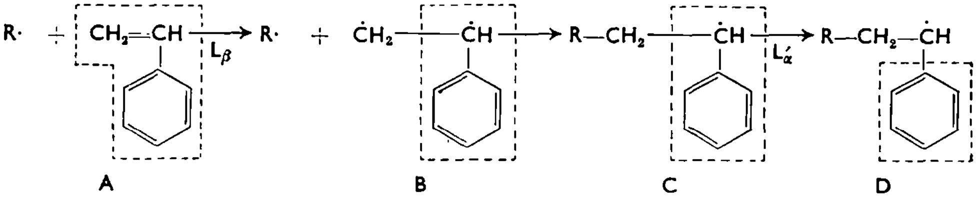
[1] K. Itoh, S. Sakai and G. Ishii, *J. Chem. Soc. Japan*, Industrial Section, to be published.

[2] W. A. Waters, *Mechanisms of Oxidation of Organic Compounds* p. 97. Methuene, London (1964).

[3] T. Alfrey and C. C. Price, *J. Polymer Sci.* **2**, 101 (1947).

[4] N. Kawabata, T. Tsuruta and J. Furukawa, *Makromol. Chem.* **51**, 70, 80 (1962).

Tsuruta *et al.*[5,6] calculated the stabilizing parameters L_α' and L_β, for alpha and beta carbon stabilization energies using Wheiand's localization method. The following model scheme for calculation was utilized in the polymerization of styrene.[6]



They estimated the L_β from the energy difference between A and B, L_α' from C and D. A correspondance between logarithms of Q and L_β, and logarithms of P and L_α' was observed. The L_β values were also correlated to the logarithms of methyl affinities proposed by Szwarc.[7]

On the other hand, Tsuruta found an important relationship between L_α' and L_β, that is, $dL_\alpha'/dL_\beta = -1{\cdot}48$. Consequently, using this relationship, it was possible to estimate approximately values for L_α' from revised Q values.

In the case of autoxidation of isopropyl compounds, $(CH_3)_2CH$—X, the tertiary hydrogen atom would be attacked mainly by the peroxy radical and $(CH_3)_2\dot{C}$—X would be formed. This tertiary radical was considered to be similar in structure to D in the preceding model of styrene polymerization. So L_α' is the most appropriate parameter for the measure of the conjugation stabilizing abilities of several substituents on alpha carbon atoms in the autoxidation of isopropyl compounds.

RESULTS AND DISCUSSION

Various isopropyl compounds were autoxidized with molecular oxygen in ampoules at 140°. The amounts of substrates [A], were determined by gas chromatography at appropriate time intervals. The observed rate constants k_0, which were calculated from the rates of decrease of substrates followed the first order kinetics generally accepted for autoxidation processes.[8] The plots of logarithms of $[A]t/[A]_0$ against time gave as expected fairly good straight lines for several isopropyl compounds. The results are summarized in Table 1.

However, as the L_α' values of methyl vinyl ketone had not been calculated, L_α' in Table 1 was extrapolated in the following manner from four conjugative monomers. Several vinyl monomers which had structures like methyl vinyl ketone were selected—methyl acrylate, methyl methacrylate, acrylonitrile and methacrylonitrile. Plotting the logarithms of their revised Q values against their L_α', a linear relationship was obtained as in Fig. 1.

Using the reported Q value of methyl vinyl ketone (3·45),[4] L_α' was estimated from Fig. 1 as being 0·972.

The logarithms of autoxidation rate constants were plotted against L_α' of the corresponding vinyl monomers and a linear relationship between them was obtained as in Fig. 2.

---

[5] T. Fueno, T. Tsuruta and J. Furukawa, *J. Chem. Soc. Japan* Pure Chemistry Section, **78**, 1075 (1957).

[6] T. Tsuruta, *Kobunshigoseihanno* p. 85. Nikkan Kogyo, Tokyo (1959).

[7] M. Szwarc, *J. Phys. Chem.* **61**, 40 (1951).

[8] Ref. 2, p. 12.

TABLE 1. THE AUTOXIDATION RATE CONSTANTS OF ISOPROPYL COMPOUNDS[a]

Substrate	Substituent	k_0 (hr^{-1})	L_α'[b]
Isopropyl methyl ketone	$—COCH_3$	0·112	(0·972)[c]
Isobutyronitrile	$—CN$	0·0562	0·839
Cumene	$—C_6H_5$	0·0465	0·721
Methyl isobutyrate	$—COOCH_3$	0·0228	0·645
Isopropyl chloride	$—Cl$	0·00590	0·477
Diisopropyl ether	$—OCH(CH_3)_2$	0·00550	1·647[d]
Isopropyl acetate	$—OOC·CH_3$	0·00532	0·445

[a] At 140°, 5·00 milimoles of substrates and 1·55 milimoles of O_2.

[b] Literature 5 (for corresponding vinyl monomers, β unit).

[c] Extrapolated from revised Q values (see text).

[d] The value of ethyl vinyl ether given in the Lit. 6.

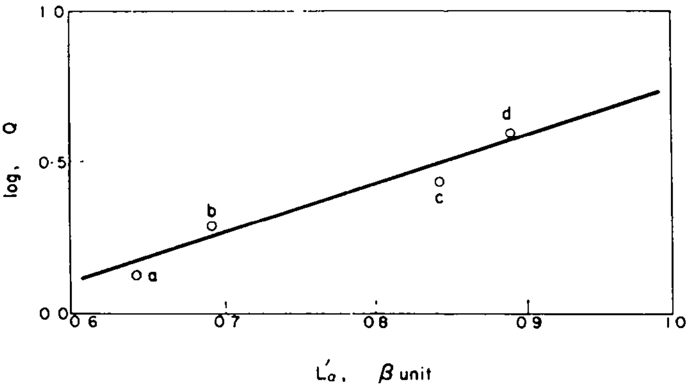


FIG. 1. The correlation between logarithms of revised Q values and L_α'.
a. Methyl acrylate, b. Methyl methacrylate, c. Acrylonitrile and d. Methacrylonitrile.

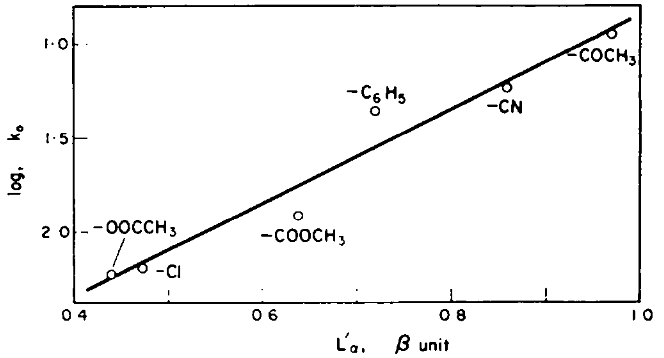
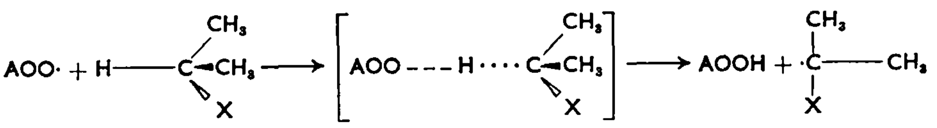


FIG. 2. The dependence of autoxidation rate constants of isopropyl compounds on L_α' at 140°. $(CH_3)_2CH—X$.

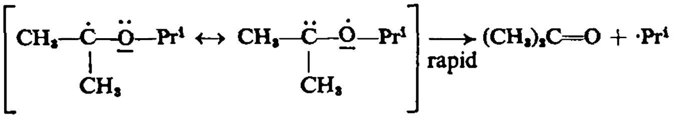
This relationship showed that the autoxidation rate constants are determined by the stability of the radical formed by hydrogen abstraction except in diisopropyl ether. The bond energies of carbon–hydrogen bonds made a minor contribution to the rates.

Recently, Kosower *et al.*[9] reported that bond energies are the dominating factor for the reaction of the 1-ethyl-4-carbmethoxypyridyl radical with various halohydrocarbons. The radical reactivity of 1-ethyl-4-carbmethoxypyridyl was thought to be extremely low and the transition state for the fission of the carbon–halogen bonds would resemble the reactants rather than the products.

But in this case, the attacking radical would mainly be the peroxy radicals $(CH_3)_2C(OO\cdot){-}X$, which would have a high reactivity, the transition state for the bond fission of the carbon–hydrogen bond was considered to be closer to the products system as in II. So the rates were determined by the stabilities of products, especially those of tertiary the radicals III.


II III

Diisopropyl ether had a lower reactivity than expected from an extremely large value of L_α'. A conjugated structure as in IV, would contribute considerably.


$$\left[\underset{\displaystyle CH_3}{CH_3{-}\dot{C}{-}\ddot{\underline{O}}{-}Pr^i} \leftrightarrow \underset{\displaystyle CH_3}{CH_3{-}\ddot{C}{-}\dot{\underline{O}}{-}Pr^i}\right] \xrightarrow[\text{rapid}]{} (CH_3)_2C{=}O + \cdot Pr^i$$

IV

So the density of unpaired electrons at the alpha carbon atom was considered to be extremely low and the alkyl–oxygen bond liable to be broken. This view would be supported by the study on the vapour phase oxidation of diethyl ether.[10] The radical formed by alpha hydrogen abstraction was shown to decompose exclusively by the fission of the ethyl–oxygen bond. So the autoxidation of isopropyl ether was thought to proceed by a mechanism different from that of other isopropyl compounds, that is, the α-peroxy isopropyl radical would not be a chain carrier. This anomalous behavior of isopropyl ether is interesting when compared with the ability of homopolymerization. Some vinyl monomers with L_α' larger than 1·0, vinylidene cyanide, 1,1-diphenylethylene, nitroethylene and ethyl vinyl ether, are known to be difficult to homopolymerize.[6] This was explained as overstabilization by substituents and further addition of monomers to polymer radical being inhibited by low radical density on the alpha carbon atom.[6]

---

[9] E. M. Kosower and I. Schrager, *J. Amer. Chem. Soc.* **86**, 5128 (1964).

[10] J. D. Waddington, *Proc. Roy. Soc.* **252A**, 260 (1959).

EXPERIMENTAL

Materials. Isopropyl methyl ketone was obtained by the method of Whitmore[11] and redistilled through a 50 cm Widmer type column (b.p. 92°). Methyl isobutyrate was prepared by acid catalysed esterification of isobutyric acid. Isopropyl chloride was prepared from isopropanol, $ZnCl_2$ and HCl according to Whaley's method.[12] Cumene, isopropyl acetate, isobutyronitrile and diisopropyl ether were commercial guaranteed reagents. All these reagents were distilled before use and their purities checked by gas chromatography.

Rate studies. Ampoules were filled with 1·55 milimoles dry O_2 at 0° and 5·00 milimoles of substrates added by means of a syringe. After sealing, the ampoules were placed in rotary mixing reactor at 140° and a mixing rate of 30 r.p.m.

The samples were analysed by gas chromatography at appropriate time intervals. The gas chromatography was performed with Yanagimoto GCG-220 model at 110°. Column (2m) of tricresyl phosphate on Cellite 545 was used. The flow rate of carrier H_2 gas was 100 ml/min.

[11] F. C. Whitmore, W. L. Evans and N. S. Rothrock, *Organic Syntheses* Coll. Vol. 2; p. 408. J. Wiley, New York (1943).

[12] J. E. Copenhaver, A. M. Whaley, *Organic Syntheses* (2nd Edition) Coll. Vol. 1; p. 142. J. Wiley, New York (1956).