

INFLUENCE OF THE ELECTROPHILIC CHARACTER ON THE REACTIVITY OF
FREE RADICALS IN SOLUTION
REACTIVITY OF ALKOXY, HYDROXY, ALKYL AND AZIDO RADICALS
IN PRESENCE OF OLEFINS

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NOT always in the field of free radicals in solution is the right importance attached to the polar characteristics of the reagents. These features are often disregarded, and the radicals considered as non-polar reagents, owing to the formal distribution of the electronic charge.

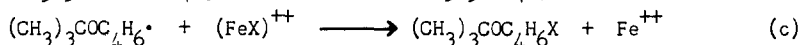
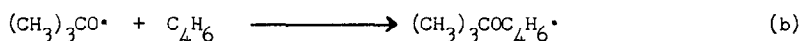
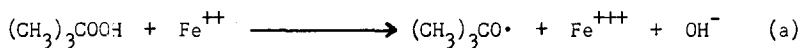
Regarding the radical attack to olefins, Walling has already pointed out how thiyl radicals, to which an electrophilic character is attributed, react more easily with styrenes having electron supplying groups in the para position.¹ On the other hand the influence of polar factors in aromatic homolytic substitutions has recently been pointed out, especially by Hey and coworkers², and long ago the importance of polar phenomena in radical copolymerization processes was noted.³ In our opinion, the influence of the polar characteristics of free radicals is of great importance in some new interactions with olefinic systems discovered by us. We have already described the behaviour of the decomposition reaction of t-butyl

¹ C. Walling, D. Seymour and K.B. Wolfstirn, J. Amer. Chem. Soc. **70**, 2559 (1948); C. Walling and W. Helmreich, J. Amer. Chem. Soc. **81**, 1144 (1959).

² G.H. Williams, Homolytic Aromatic Substitution. Pergamon Press, London (1960).

³ C. Walling, Free Radicals in Solution p. 132. John Wiley, New York (1957).

hydroperoxide with ferrous and cuprous salts in presence of butadiene and chlorine, azido and thiocyan ions;⁴ this reaction was outlined by us in the following manner:



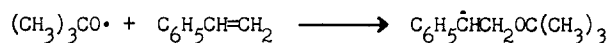
The last step of the process (c), i.e. the interaction of a carbon free radical with the anion coordinated with the metallic salt, is connected with the interpretation of Sandmeyer's reaction by Waters⁵ and with a group of organic peroxide reactions recently described by one of us, in which carbon free radicals, arising from decomposition of peroxides, give rise to products analogous to those obtained in Sandmeyer's reaction.⁶ Other conjugated olefins such as cyclopentadiene and substances with some dienic character such as furan (in this case the reaction is further complicated by the easy hydrolysis and alcoholysis of 1-4 addition products) behave similarly to butadiene. In carrying out the decomposition of the hydroperoxide under the same conditions in the presence of styrene we noted an unusual fact. While in the presence of chlorine ions the reaction occurred normally and the chlor-ether, $\text{C}_6\text{H}_5\text{CHClCH}_2\text{OC}(\text{CH}_3)_3$, was obtained as the only reaction product (obviously by means of a mechanism like that outlined above for the butadiene), when the reaction was conducted in the presence of sodium-azide a mixture of azide-ether, $\text{C}_6\text{H}_5\text{CH}(\text{N}_3)\text{CH}_2\text{OC}(\text{CH}_3)_3$,

⁴ F. Minisci, R. Galli and U. Pallini, *Gazz. Chim. Ital.* **91**, 1023 (1961).

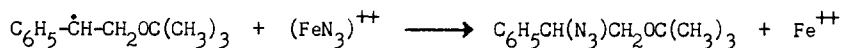
⁵ D.C. Nonhebel and W.A. Waters, *Proc. Roy. Soc.* **A242**, 16 (1957).

⁶ F. Minisci, *Gazz. Chim. Ital.* **89**, 626, 1910, 1921, 1941, 2428, 2438 (1959); **90**, 1299, 1307, 1318 (1960); J.K. Kochi [*Tetrahedron* **18**, 483 (1962)] speaks of an analogy in the catalytic action of copper salt between the Sandmeyer and Meerwein reactions of diazonium salts and the peroxide reactions. This analogy was pointed out by one of us in 1958 [F. Minisci, *Rend. Accad. Naz. Lincei* serie VIII, vol. XXV, fasc. 6, 538 (1958) and following papers].

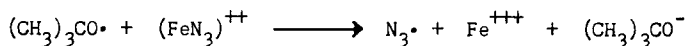
and diazide, $C_6H_5CH(N_3)CH_2N_3$, was obtained. In our opinion this fact must be connected with the strong electrophilic character of the alkoxy radical, which is easily able to attack olefinic systems with high electron density and rather less easily conjugated olefinic systems with electron-withdrawing groups. In this case two interactions of t-butoxy radical should take place at the same time, the former with styrene



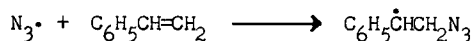
followed by the azide-ether formation,



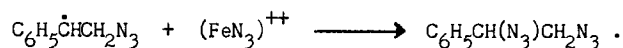
and the latter with the azido group coordinated with the iron salt



and yielding an azido radical, which would be able to attack the ethylenic bond,

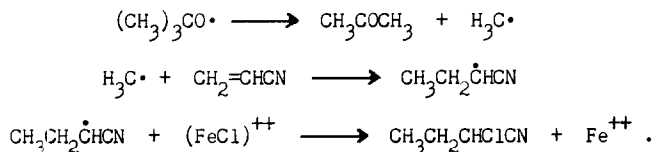


and then form the diazide



Obviously this is a simplified scheme which tends to point out the homolytic character of the interaction, since it can be reasonably supposed that interaction of the metallic salt with the ethylenic bond also occurs. In the case of olefins conjugated with strong electron-withdrawing groups we observed a greatly decreased reactivity of the alkoxy radical, so that in the t-butyl hydroperoxide decomposition in the presence of the Fe^{++}/Fe^{+++} system, chlorine ions and acrylonitrile, a strongly decreased reactivity is observed compared with the other conjugated olefins considered above and α -chlor-butyrionitrile is obtained as main reaction product. The strong electrophilic character of t-butoxy radical does not, in this case, lead to interaction with an "electron-deficient" ethylenic bond, but to re-arrangement resulting in a much less electrophilic methyl radical. On the

contrary it can be reasonably maintained that the nucleophilic character of the $\text{H}_3\text{C}\cdot$ radical is prevalent over the electrophilic one, since the tendency to lose electrons, $\text{H}_3\text{C}\cdot \longrightarrow \text{CH}_3^+ + e$, is greater than that to gain electrons, $\text{H}_3\text{C}\cdot + e \longrightarrow (\text{CH}_3\cdot)^-$,⁷ and is responsible for the reaction path*



This behavior is analogous to that recently pointed out by one of us in the case of haloalkylation of acrylic derivatives by means of 1-hydroxyhydroperoxides, >C(OH)OOH ,⁸ and enables us to understand better the addition reactions of CCl_4 and CHCl_3 with acrylonitrile carried out in this laboratory, from which α,γ,γ -tetrachlorobutyronitrile, $\text{CCl}_3\text{CH}_2\text{CHClCN}$, and α,γ -trichlorobutyronitrile, $\text{CHCl}_2\text{CH}_2\text{CHClCN}$, are obtained as main products.⁹ These last reactions were formerly interpreted as radical chain processes paralleling the radical addition of halogen derivatives to olefins. This former interpretation, although pointing out the radical character, was inadequate in that it offered no satisfactory explanation of the fact that radical addition of chloroform to olefins occurs, as a rule, according to the scheme,¹⁰ $\text{CHCl}_3 + \begin{array}{c} | & | \\ \text{C} & - & \text{C} \\ | & | \end{array} \longrightarrow \text{CCl}_3\begin{array}{c} | \\ \text{C} \\ | \end{array}\text{CH}$, while under our reaction conditions with acrylonitrile α,γ -trichlorobutyronitrile was obtained. These

* Recently L. Kerk, A. Stefani and M. Szwarc [*J. Amer. Chem. Soc.* **83**, 3008 (1961)] have pointed out how the affinity of methyl radicals towards conjugated olefins increases with increasing electron-withdrawing power of conjugated groups.

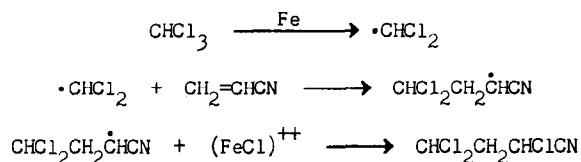
⁷ D.J. Mackinnon and W.A. Waters, *J. Chem. Soc.* 323 (1953).

⁸ F. Minisci and U. Pallini, *Gazz. Chim. Ital.* **91**, 1030 (1961).

⁹ M. De Malde, F. Minisci, E. Volterra and A. Quillico, *Chim. & Ind.* 371 (1956).

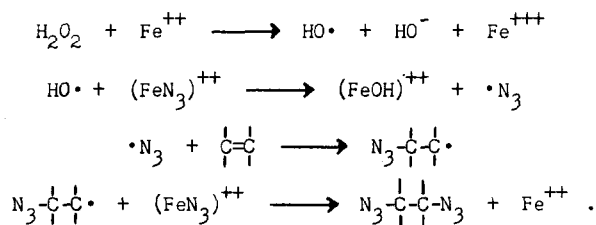
¹⁰ M.S. Kharasch, E.V. Jensen and W.H. Urry, *J. Amer. Chem. Soc.* **69**, 110 (1947).

new haloalkylation reactions of acrylonitrile, together with the fact that the reactions between acrylonitrile and CCl_4 and CHCl_3 were carried out in presence of iron, lead us now to consider the latter as oxidation-reduction and not radical-chain processes.



The conviction that the reaction path between styrene and sodium azide was determined by the electrophilic character of the t-butoxy radical led us also to increase the electrophility of the oxygen radical and to form $\text{HO}\cdot$ radicals in the same reaction system, by using hydrogen peroxide instead of hydroperoxide; in this manner only the diazide was obtained. Moreover the reaction is not limited to styrene and conjugated olefins, as butadiene and cyclopentadiene for example, but is effective in general also for non-conjugated olefins (e.g. 2-pentene, 1-hexene, cyclohexene).

Accordingly, this is a new general method of adding two azido groups to the double bond of olefins, based upon the hydrogen peroxide decomposition with ferrous sulphate in presence of olefin and alkaline azide. The series of interactions can be outlined as follows:



According to this interpretation, the hydroxyl radical, owing to his very strong electrophilic character, would not interact with the olefin, but with the azido ion coordinated with the iron salt. Also the azido radical

$\cdot\text{N}_3$ shows an electrophilic character, although this is not so strong as that of the hydroxyl radical $\cdot\text{OH}$, and thus the reaction will not be favoured in the case of ethylenic bonds conjugated with strong electron-withdrawing groups. Accordingly, the results obtained with 1-hexene, cyclohexene or butadiene are much better than those with acrylonitrile. Also in this case it is reasonable to suppose that an interaction between iron salt and olefin will influence the behaviour of the reaction.

From the whole of the interactions considered above, it is plain that the electrophilic character of the reacting radicals, together with the resonance stabilization of intermediate radicals, result in a remarkable influence over the behaviour of reaction, although, considering the coordinating ability of the metallic ion, one should speak more properly in these cases of "coordinated radical mechanisms".

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