Free-Radical Additions to Olefins in the Presence of Redox Systems


Francesco Minisci

Istituto di Chimica del Politecnico, Milano, Italy

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1937 was a big year in the organic chemistry of free radicals. Kharasch and coworkers[1] discovered the "peroxide effect" which accounts for the anti-Markovnikov addition of HBr to olefins and put forward the now generally accepted free-radical mechanism. Hey and Waters[2] published their famous review article in which they outlined radical mechanisms for several organic reactions, including the abnormal addition of HBr to alkenes. Flory[3] suggested the radical-chain mechanism for vinyl polymerization which is now the basic theoretical premise of a major industry.

Stoichiometrically simple additions to terminal alkenes can be represented as in eq 1, in which the

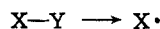$$X-Y + CH_2=CHR \longrightarrow XCH_2-CHRY \qquad (1)$$
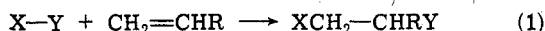
reagent added is symbolized X-Y. Reagents which add to olefins by a radical mechanism include hydrogen halides, hydrocarbons, polyhaloalkanes, alcohols, ethers, amines, aldehydes, ketones, aliphatic acids and esters, and compounds of sulfur, phosphorus, silicon, tin, germanium, and other elements.[4]

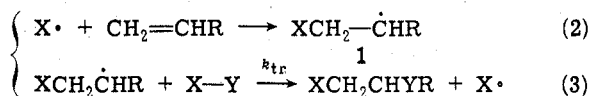The radical-addition mechanism is a complex sequence of steps, as shown in Scheme I.

Initiation is the step in which radicals are first generated to participate in the chain mechanism. It may involve thermal or photochemical homolysis, as indicated in Scheme I, or radicals may be generated by radiolysis or redox reactions. Inasmuch as most of the actual transformation of chemicals occurs in the
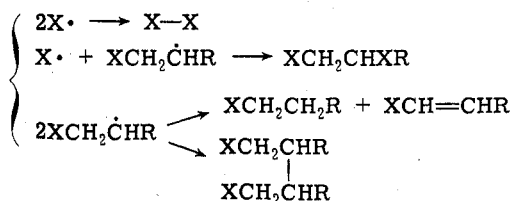
Scheme I

Initiation

$$X-Y \longrightarrow X\cdot$$

Propagation

$$\begin{cases} X\cdot + CH_2=CHR \longrightarrow XCH_2-\dot{C}HR & (2) \\ & \qquad\qquad\qquad 1 \\ XCH_2\dot{C}HR + X-Y \xrightarrow{k_{tr}} XCH_2CHYR + X\cdot & (3) \end{cases}$$

Termination

$$\begin{cases} 2X\cdot \longrightarrow X-X \\ X\cdot + XCH_2\dot{C}HR \longrightarrow XCH_2CHXR \\ 2XCH_2\dot{C}HR \diagup\!\!\!\!\!\diagdown \begin{matrix} XCH_2CH_2R + XCH=CHR \\ XCH_2CHR \\ | \\ XCH_2CHR \end{matrix} \end{cases}$$

propagation steps (if the chain is long), the initial source of radicals has little influence on the nature of the reaction products.

A significant complication in additions according to eq 1 arises from the circumstance that the radical formed in step 2 may not only abstract atom Y as in step 3 but also add to another olefin molecule as shown in eq 4. If the propensity of such a radical to

$$XCH_2CHR\cdot + CH_2=CHR \xrightarrow{k_p} XCH_2CHRCH_2CHR\cdot \qquad (4)$$
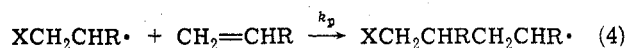
add to an olefin molecule is much greater than to abstract Y from XY, the result is telomerization or ultimately vinyl polymerization. Whether the overall result is addition or telomerization depends on the chemical characteristics of molecule XY, of the olefin, and of the radical $XCH_2CHR\cdot$.

Other features of a system may thwart a desired addition according to eq 1. Even if abstraction of Y from XY occurs readily in step 3, the resulting radical $X\cdot$ may be too unreactive to continue the propagation sequence in step 2. A different kind of problem is that the reagent to provide a desired pair of groups, X and Y, may not exist or may not be stable under reaction conditions. For example, if X and Y are both to be azido groups, carrying out an addition according to eq 1 is impossible because of the unavailability of N_6.

Many of these problems can be overcome if a redox system is present in the addition reaction mixture. This is usually supplied by having present a metal salt such as Fe^{3+} or Cu^{2+}. Such salts can greatly affect the course of radical additions to olefins and the nature of the products obtained. Sometimes, moiety X can be supplied to the olefin from one component of a redox system and moiety Y from another component or from a third reagent.

Returning specifically to the problem of competition between steps 3 and 4, we see that a high chain-transfer constant, k_{tr}/k_p, leads to high yields of adduct according to eq 1, whereas a low k_{tr}/k_p ratio causes formation of a chain polymer. A redox system generally does not affect k_p, but it can cause transfer of moiety Y or of another group to radical adduct 1. If the rate of the redox-promoted process is represented by k_{tr}', and $k_{tr}' > k_{tr}$, the chain-transfer constant will be increased.

Francesco Minisci is Professor of Chemistry at the Politecnico of Milan. He was born in Italy in 1930, and studied at the University of Bologna for his university degree. He has been on the research staff of Montecatini, as well as Professor of Industrial Organic Chemistry at the University of Parma. His research interests include various aspects of free-radical chemistry, mainly synthetic developments and polar effects in free-radical reactions.

(1) M. S. Kharasch, H. Engelmann, and F. R. Mayo, *J. Org. Chem.*, 2, 288 (1937).

(2) D. H. Hey and W. A. Waters, *Chem. Rev.*, 21, 169 (1937).

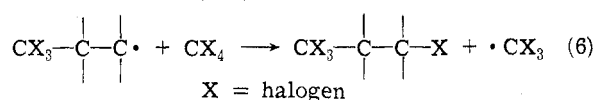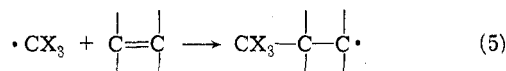(3) P. J. Flory, *J. Am. Chem. Soc.*, 59, 241 (1937).

(4) G. Sosnovsky, "Free Radical Reactions in Preparation Organic Chemistry", Macmillan, New York, N.Y., 1964; C. Walling and E. S. Huyser, *Organic React.*, 13, 91 (1963); F. W. Stacey and J. F. Harris, *ibid.*, 13, 150 (1963).

Two main types of redox free-radical additions are now considered: (a) inclusion of redox systems into the propagation steps of conventional free-radical chain additions, and (b) free-radical additions primarily determined by redox systems and impracticable by conventional chain processes.

Free-Radical Chain Additions to Olefins Modified by Redox Systems

Some significant examples of addition emphasize the main theoretical and synthetic aspects of these processes.

Polyhaloalkanes. The free-radical addition of polyhalomethanes to olefins is of wide synthetic application and has received a great deal of study in radical-addition reactions.[4] The propagation steps are given by eq 5 and 6. The yields of the single addition

$$\cdot CX_3 + \underset{|}{\overset{|}{C}} = \underset{|}{\overset{|}{C}} \longrightarrow CX_3 - \underset{|}{\overset{|}{C}} - \underset{|}{\overset{|}{C}} \cdot \qquad (5)$$

$$CX_3 - \underset{|}{\overset{|}{C}} - \underset{|}{\overset{|}{C}} \cdot + CX_4 \longrightarrow CX_3 - \underset{|}{\overset{|}{C}} - \underset{|}{\overset{|}{C}} - X + \cdot CX_3 \quad (6)$$

$$X = \text{halogen}$$

product are high in the reactions of CCl_3Br with alkenes, in which the weak bond C–Br is involved in the transfer reaction (eq 6). However, with less reactive polyhalomethanes such as CCl_4 and $CHCl_3$, telomer formation is a serious complication in additions involving simple olefins and much more serious with polymerizable vinyl monomers (high value of k_p).

In 1956, in our laboratories,[5] attempted thermal polymerizations of acrylonitrile in CCl_4 and $CHCl_3$ in a steel autoclave yielded two unusual results: formation of a considerable amount of monoadduct between CCl_4 and acrylonitrile, $CCl_3CH_2CHClCN$, and formation of the monoadduct $CHCl_2CH_2CHClCN$ with $CHCl_3$.

These results were unexpected because the transfer constants (k_{tr}/k_p) of CCl_4 and $CHCl_3$ are not high enough to prevent polymerization of acrylonitrile and the usual addition of $CHCl_3$ to alkenes involves abstraction of hydrogen rather than chlorine in the transfer reaction (eq 6). (The usual free-radical chain addition would give $CCl_3CH_2CH_2CN$).

In 1961, on the grounds of analogous redox haloalkylations of acrylonitrile, the author[6] suggested by way of explanation a mechanism in which iron chlorides, arising from corrosion of the autoclave (eq 7 and 8), played the main role.

$$2CCl_4 + Fe \longrightarrow 2 \cdot CCl_3 + FeCl_2 \qquad (7)$$

$$FeCl_2 + CCl_4 \longrightarrow FeCl_3 + \cdot CCl_3 \qquad (8)$$
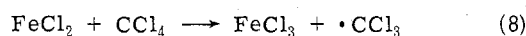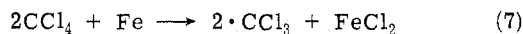
The transfer constant (k_{tr}'/k_p) of $FeCl_3$, much higher than that of CCl_4 and $CHCl_3$, prevents acrylonitrile from undergoing extensive polymerization or telomerization (eq 9).

$$CCl_3CH_2\overset{\cdot}{C}HCN + FeCl_3 \overset{k_{tr}'}{\longrightarrow}$$

$$CCl_3CH_2CHClCN + FeCl_2 \quad (9)$$
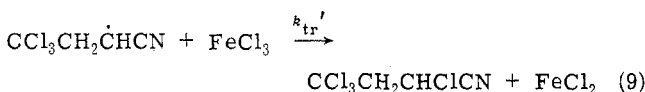
The reoxidation of $FeCl_2$ by CCl_4 (eq 8) establishes a redox chain. A similar step with $CHCl_3$ explains the nature of the product obtained when it is the reagent added (eq 10).
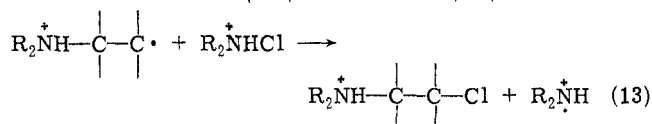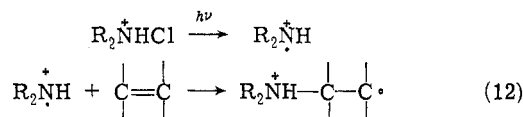
$$CHCl_3 + FeCl_2 \longrightarrow \cdot CHCl_2 + FeCl_3 \qquad (10)$$
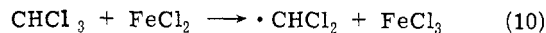
The reactions of CCl_4, $CHCl_3$, and a variety of polyhaloalkanes with olefins catalyzed by iron and copper salts have been extensively investigated, mainly by Asscher and coworkers[7] and by Freidlina and coworkers,[8] who have provided numerous data substantially supporting the mechanism of eq 8 and 9. The great advantage offered by the redox chain addition of polyhaloalkanes to olefins in comparison with conventional chain addition (e.g., initiated by peroxide) is the minimization or the elimination of polymer or telomer formation even with polymerizable olefins (vinyl monomers). Moreover, the redox chain can change the nature of the adduct, as in the case of $CHCl_3$, and it can allow the addition of compounds of general structure $RCHXCCl_3$,[8] which fail to react with unsaturated compounds via rupture of the CCl bond in CCl_3 group in the presence of conventional radical-forming agents, such as peroxides, azo compounds, or ultraviolet light.

A typical example is the preparation of 1,1,3,3-tetrachloropropane, an interesting intermediate which can replace malondialdehyde in heterocyclic syntheses. It was obtained in high yields (82% based on C_2H_3Cl or 91% on $CHCl_3$), simply and inexpensively, from $CHCl_3$ and vinyl chloride[9] (eq 11). The conventional free-radical chain process does

$$CHCl_3 + CH_2{=}CHCl \xrightarrow{\text{Fe}^{2+} \text{ or } \text{Cu}^+} CHCl_2CH_2CHCl_2 \quad (11)$$
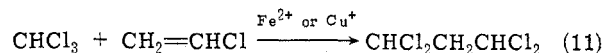
not work because the low transfer constant of $CHCl_3$ cannot prevent vinyl chloride from polymerizing, and in any case it would have led to 1,1,1,3-tetrachloropropane.

***N*-Chloramines.** Free-radical chain addition of protonated *N*-chloramines to olefins takes place according to eq 12 and 13.[10] A severe limitation of this

$$R_2\overset{+}{N}HCl \xrightarrow{h\nu} R_2\overset{+}{N}H$$

$$R_2\overset{+}{N}H + \underset{|}{\overset{|}{C}}{=}\underset{|}{\overset{|}{C}} \longrightarrow R_2\overset{+}{N}H - \underset{|}{\overset{|}{C}} - \underset{|}{\overset{|}{C}} \cdot \quad (12)$$

$$R_2\overset{+}{N}H - \underset{|}{\overset{|}{C}} - \underset{|}{\overset{|}{C}} \cdot + R_2\overset{+}{N}HCl \longrightarrow$$

$$R_2\overset{+}{N}H - \underset{|}{\overset{|}{C}} - \underset{|}{\overset{|}{C}} - Cl + R_2\overset{+}{N}H \quad (13)$$

process is competition with electrophilic chlorination of the olefins (eq 14). Thus the free-radical amino chlorination is effective with conjugated olefins, such

$$R_2\overset{+}{N}HCl + \underset{|}{\overset{|}{C}}{=}\underset{|}{\overset{|}{C}} \longrightarrow R_2NH + Cl - \underset{|}{\overset{|}{C}} - \underset{|}{\overset{|}{C}}{}^+ \quad (14)$$

$$Cl - \underset{|}{\overset{|}{C}} - \underset{|}{\overset{|}{C}}{}^+ + ROH \longrightarrow Cl - \underset{|}{\overset{|}{C}} - \underset{|}{\overset{|}{C}} - OR + H^+$$

(5) M. DeMaldè, F. Minisci, U. Pallini, E. Volterra, and A. Quilico, *Chim. Ind. (Milan)*, 38, 371 (1956).

(6) (a) F. Minisci and U. Pallini, *Gazz. Chim. Ital.*, 91, 1030 (1961); (b) F. Minisci and R. Galli, *Tetrahedron Lett.*, 533 (1962); (c) F. Minisci and R. Galli, *Chim. Ind. (Milan)*, 45, 1400 (1963).
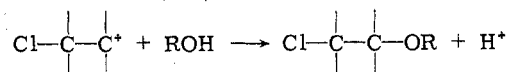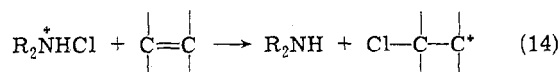
(7) M. Asscher and D. Vofsi, *J. Chem. Soc.*, 1887, 3921 (1963); *J. Chem. Soc. B*, 947 (1968); A. Orochov, M. Asscher, and D. Vofsi, *J. Chem. Soc., Perkin Trans. 2*, 1000 (1973).

(8) R. Kh. Freidlina and E. C. Chukovskaya, *Synthesis*, 477 (1974), and references quoted therein.

(9) F. Minisci and R. Galli, Italian Patent 700,129 (1963).

(10) R. S. Neale and R. L. Hinman, *J. Am. Chem. Soc.*, 85, 2667 (1963).

as butadiene, and with weakly deactivated olefins such as $CH_2=CHCH_2X$, where X is an electron withdrawing group. It is unsuccessful with simple olefins and strongly deactivated olefins for opposite polar reasons. Simple olefins preferentially undergo electrophilic chlorination while olefins conjugated with electron-withdrawing groups ($CH_2=CHX$, X = CN, COOR, COR) do not react owing to the strong electrophilic character of the amino radical.[11]
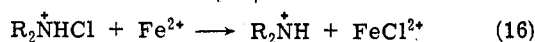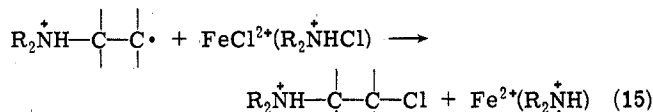
A redox process obviates the difficulties with simple olefins. Since the reaction of *N*-chloramines with ferrous salt (eq 16) is faster than electrophilic chlorination of the olefin, the redox chain of eq 12, 15, and 16 operates effectively.[12] A different solution of

$$R_2\overset{+}{N}H-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}\cdot + FeCl^{2+}(R_2\overset{+}{N}HCl) \longrightarrow$$

$$R_2\overset{+}{N}H-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-Cl + Fe^{2+}(R_2\overset{+}{N}H) \quad (15)$$

$$R_2\overset{+}{N}HCl + Fe^{2+} \longrightarrow R_2\overset{+}{N}H + FeCl^{2+} \quad (16)$$

this problem has been achieved by redox addition of unprotonated *N*-chloramines which occurs via propagation steps analogous to eq 12, 15, and 16, with the difference that the *N*-chloramines and amino radicals are not protonated.[6c,11,13,14] Unprotonated *N*-chloramines generally do not undergo conventional free-radical chain additions to olefins because propagation steps 12 and 13 are both sluggish. A further advantage of adding the unprotonated *N*-chloramines is that under the reaction conditions they do not participate in electrophilic chlorination of the double bond.

The reactions of protonated and unprotonated *N*-chloramines also result in adducts of different stereochemistry. Thus, addition to cyclohexene in acidic medium gave a mixture of cis and trans products, whereas in nonacidic solution with unprotonated *N*-chloramine mainly the cis isomer was obtained. This stereoselectivity was attributed to coordination of the unprotonated amino group with the ferric salt which is mainly responsible for the chlorine atom transfer[13,15] (eq 17). The protonated amino radical
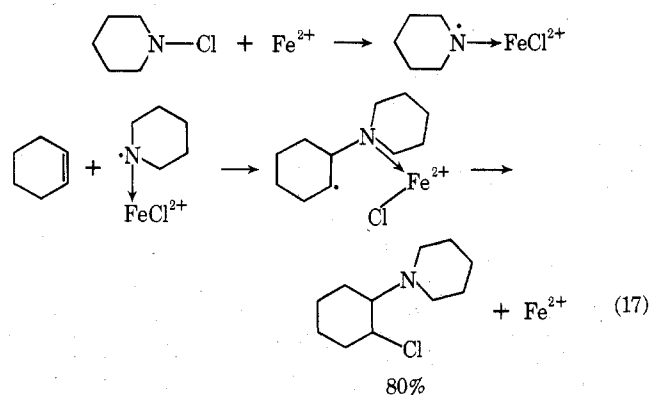
would not be expected to form such a complex, and therefore a less stereospecific reaction would occur.

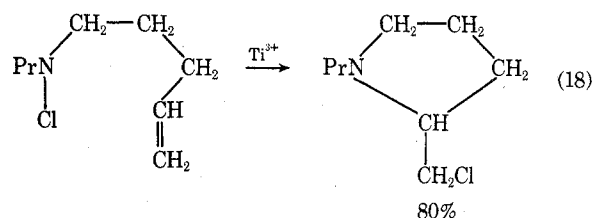(11) F. Minisci and R. Galli, *Chim. Ind. (Milan)*, 46, 546 (1964).

(12) F. Minisci, R. Galli, and M. Cecere, *Tetrahedron Lett.*, 3163 (1966).

(13) F. Minisci, R. Galli, and G. Pollina, *Chim. Ind. (Milan)*, 47, 736 (1965).

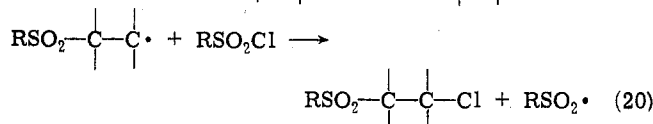(14) F. Minisci, *Chim. Ind. (Milan)*, 49, 705 (1967).

(15) F. Minisci, R. Galli, and M. Cecere, *Chim. Ind. (Milan)*, 48, 347 (1966).

Ring closure to pyrrolidine derivatives (eq 18) has

been achieved by intramolecular redox additions in unsaturated *N*-chloramines.[16]

Sulfonyl Chlorides. Free-radical chain additions of nonactivated sulfonyl chlorides to olefins (eq 19 and 20), initiated by peroxides, are successful only in

$$RSO_2\cdot + \overset{|}{C}=\overset{|}{C} \rightleftharpoons RSO_2-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}\cdot \quad (19)$$

$$RSO_2-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}\cdot + RSO_2Cl \longrightarrow$$

$$RSO_2-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-Cl + RSO_2\cdot \quad (20)$$
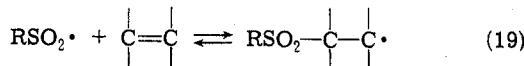
the case of strained olefins such as norbornene and norbornadiene.[17] Addition to unstrained olefins proceeds less readily because eq 19 is reversible and eq 20 is not fast enough to shift the equilibrium to the right.

The addition becomes easy in the presence of cupric salt,[18] according to a redox chain involving prominently steps 21 and 22. The very fast process

$$PhSO_2Cl + CuCl \longrightarrow PhSO_2\cdot + CuCl_2 \quad (21)$$

$$PhSO_2\cdot + CH_2=CH_2 \longrightarrow PhSO_2CH_2CH_2\cdot$$

$$PhSO_2CH_2CH_2\cdot + CuCl_2 \longrightarrow$$

$$PhSO_2CH_2CH_2Cl + CuCl \quad (22)$$

$$97\%$$
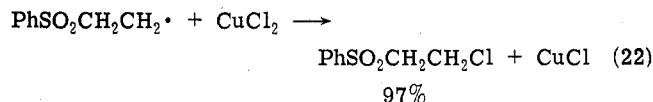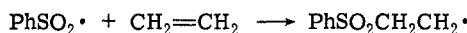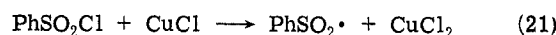
(eq 22) is responsible for shifting equilibrium 19 to the right.

Free-Radical Redox Additions to Olefins Impracticable by Conventional Chain Processes

Three principal fates for the radical adduct **1**, $XCH_2\dot{C}HR$ (cf. eq 2), can be envisaged.

(a) Radical adduct **1** selectively reacts with a metal salt in a redox chain process. A catalytic amount of metal salt is required. The two main types of interactions of alkyl radicals with metal salts are the selective transfer of an anionic group bonded to the metal (eq 23), which is mechanistical-

$$R\cdot + MY^+ \longrightarrow R-Y + M^+ \quad (23)$$

$$M^+ = Fe^{2+}, Cu^+$$
$$Y = Cl, Br, I, CN, SCN, N_3, S_2O_3^-, SC(S)OR$$
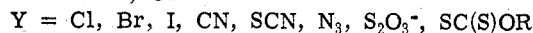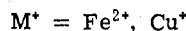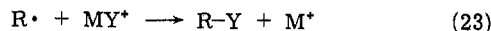
ly similar to the Sandmeyer reaction in the aliphatic series,[19] and selective oxidation of the alkyl radical to a carbonium ion (eq 24) and its further reactions

(16) J. M. Surzur, P. Tordo, and L. Stella, *Bull. Soc. Chim. Fr.*, 111, 115 (1970).

(17) S. J. Cristol and J. A. Reeder, *J. Org. Chem.*, 26, 2182 (1961).

(18) M. Asscher and D. Vofsi, *J. Chem. Soc.*, 4962 (1964); J. Sinureich and M. Asscher, *J. Chem. Soc., Perkin Trans. 1*, 1543 (1972).

(19) F. Minisci, *Angew. Chem.*, 70, 599 (1958); F. Minisci, *Gazz. Chim. Ital.*, 89, 626, 1910, 2428 (1959); F. Minisci and A. Portolani, *ibid.*, 89, 1922, 1941 (1959); F. Minisci and U. Pallini, *ibid.*, 89, 2438 (1959); F. Minisci and G. Belvedere, *ibid.*, 90, 1299 (1960); F. Minisci, *ibid.*, 90, 1307 (1960).

$$R\cdot + M^{2+} \longrightarrow R^+ + M^+ \qquad (24)$$

$$M^{2+} = Cu^{2+}, Mn^{3+}, Ce^{4+}, etc.$$

$$R^+ \longrightarrow R_{-H} + H^+ \qquad (25)$$

$$R^+ + Y-H \longrightarrow R-Y + H^+ \qquad (26)$$

$$Y = RO, HO, RCOO$$
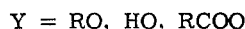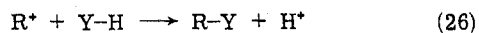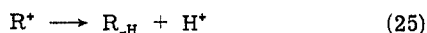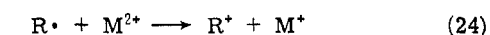
(eq 25 and 26).[20] J. K. Kochi[21] has extensively investigated mechanistic aspects of these two processes, and has called the first (eq 23) "ligand transfer" and the second (eq 24) "electron-transfer." All the redox chains discussed in the preceding section involve a ligand transfer of a chlorine atom.

(b) Radical adduct 1 selectively reacts with a metal salt of the redox system or with a different trap in a non-chain process. A stoichiometric amount of metal salt is required.

(c) The radic adduct 1, as a result of its stability, gives good yields of dimerization products. A stoichiometric amount of metal salt is required in a non-chain process also in this case.

These three processes will be illustrated by some significant redox additions of carbon-, nitrogen-, and oxygen-centered free radicals to olefins.

Carbon Free Radicals. General Scheme II accounts for a chain redox addition of carbon free radi-

Scheme II

$$S + M^+ \longrightarrow R\cdot + M^{2+}$$

$$R\cdot + \overset{|}{C}=\overset{|}{C} \longrightarrow R-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}\cdot$$
$$2$$

$$R-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}\cdot + MY^+ \longrightarrow R-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-Y + M^+$$

$$M^+ = \overset{+}{C}u \text{ or } Fe^{2+}; S = \text{organic oxidant}; Y = \text{halogen}$$

cals to olefins involving a ligand-transfer process (a). The reaction has been accomplished with aliphatic and aromatic carbon free radicals leading to haloalkylation and haloarylation of the double bond. The Meerwein reaction of arenediazonium salts is a classical example of this process (Scheme III).[22]

Scheme III

$$p\text{-}NO_2C_6H_4N_2Cl + CuCl \longrightarrow p\text{-}NO_2C_6H_4\cdot + N_2 + CuCl_2$$

$$p\text{-}NO_2C_6H_4\cdot + CH_2{=}CHCN \longrightarrow p\text{-}NO_2C_6H_4CH_2\overset{\cdot}{C}HCN$$

$$p\text{-}NO_2C_6H_4CH_2\overset{\cdot}{C}HCN + CuCl_2 \longrightarrow$$
$$p\text{-}NO_2C_6H_4CH_2CHClCN + CuCl$$
$$91\%$$
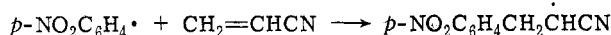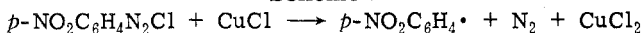
Hydroperoxides of phenylhydrazones were used as sources of aryl radicals (eq 27) in an analogous reac-
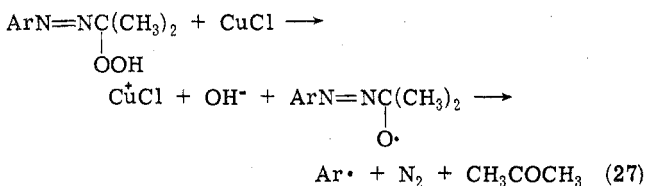
$$ArN{=}N\overset{|}{\underset{OOH}{C}}(CH_3)_2 + CuCl \longrightarrow$$

$$\overset{+}{C}uCl + OH^- + ArN{=}N\overset{|}{\underset{O\cdot}{C}}(CH_3)_2 \longrightarrow$$

$$Ar\cdot + N_2 + CH_3COCH_3 \qquad (27)$$

tion;[23] the general character of the process is probably as shown in eq 27.

Peroxides were also used as sources of alkyl radicals (eq 28[24] and 29[6a]) in haloalkylations, which

$$(CH_3)_3COOH + Fe^{2+} \longrightarrow Fe^{3+} + OH^- + (CH_3)_3CO\cdot \longrightarrow$$
$$CH_3\cdot + CH_3COCH_3 \quad (28)$$

$$+ Fe^{2+} \longrightarrow Fe^{3+} + OH^- +$$
$$\cdot CH_2(CH_2)_4COOH \quad (29)$$
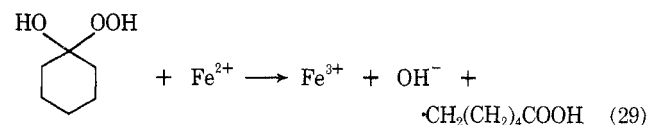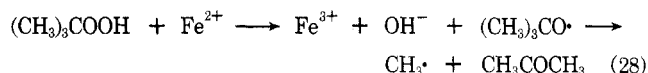
mechanistically reproduce the Meerwein reaction in aliphatic series.

The main limitation of the general process of Scheme II is the fact that R· is a carbon free radical, as is the radical adduct 2, and it can undergo a ligand-transfer process (the Sandmeyer reaction in the case of arendiazonium salts), competing with addition to the alkene (eq 30).

$$R\cdot + MY^+ \longrightarrow R-Y + M^+ \qquad (30)$$
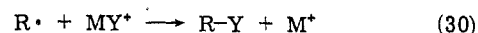
The process is therefore suitable only with reactive conjugated olefins. The limitation is more severe with alkyl than with aryl radicals because the radical adduct 2 is an alkyl radical as well. In fac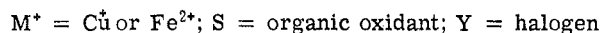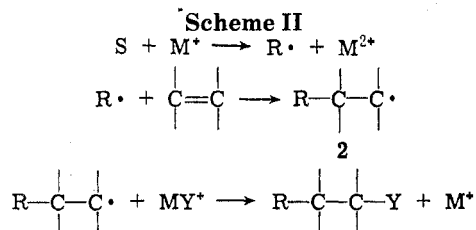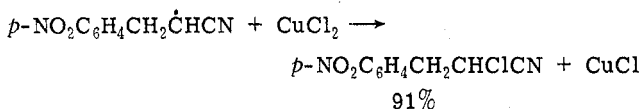t, the reaction with alkyl radicals is synthetically significant only when the olefinic double bond is conjugated with electron-withdrawing groups, owing to the nucleophilic character of the alkyl radicals. The ligand-transfer process is not very sensitive to the polar characteristics of the carbon free radicals, while the rate of addition to olefins is considerably affected.

In contrast, oxidation by electron transfer is very sensitive to the nucleophilicities of the carbon free radicals, and redox chain additions become important only when the nucleophilicities of the carbon free radicals involved are different. The alternating addition of alkyl radicals to conjugated olefins is a significant example of this behavior (Scheme IV).[25]

Scheme IV

$$\text{peroxide} + Cu^+ \longrightarrow R\cdot + Cu^{2+}$$

$$R\cdot + CH_2{=}CHX \longrightarrow RCH_2\overset{\cdot}{C}HX$$
$$3 \qquad\qquad\qquad 4$$

$$RCH_2\overset{\cdot}{C}HX + CH_2{=}CHY \longrightarrow RCH_2CHXCH_2\overset{\cdot}{C}HY$$
$$5 \qquad\qquad\qquad\qquad 6$$

$$RCHCHXCH_2\overset{\cdot}{C}HY + Cu^{2+} \longrightarrow RCH_2CHXCH_2\overset{+}{C}HY + Cu^+$$

$$RCH_2CHXCH_2\overset{+}{C}HY + R'OH \longrightarrow$$
$$RCH_2CHXCH_2CHYOR' + H^+$$

$$R\cdot = \text{alkyl radical}; X = CN, COOR, COR; Y = Ph,$$
$$CH{=}CH_2; R' = H, \text{alkyl, acyl}$$
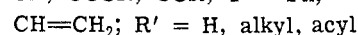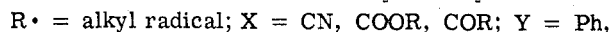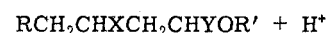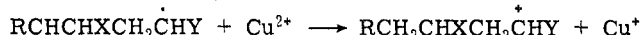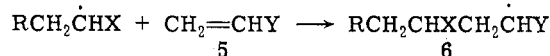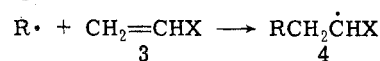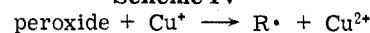
Intramolecular interaction takes place when X is a carboxylic group (eq 31).

$$RCH_2\overset{}{\underset{\overset{|}{COOH}}{C}}HCH_2\overset{+}{C}HY \longrightarrow RCH_2\overset{}{\underset{\overset{|}{CO}}{C}}H{-}CH_2{-}\overset{}{\underset{\overset{|}{O}}{C}}HY + H^+ \quad (31a)$$

(20) J. K. Kochi, *J. Am. Chem. Soc.*, 85, 1958 (1963); J. K. Kochi, A. Bemis, and C. L. Jenkins, *ibid.*, 90, 4038, 4616 (1968).

(21) J. K. Kochi, "Free Radicals", Vol. I, Wiley, New York, 1973, p 591. N.Y.,

(22) Reference 21, p 666.
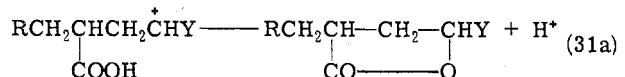
(23) F. Minisci, *Atti Accad. Naz. Lincei, Cl. Sci. Fis., Mat. Nat., Rend.*, [8] 25, 538 (1958); F. Minisci and U. Pallini, *Gazz. Chim. Ital.*, 90, 1318 (1960).

(24) F. Minisci and R. Galli, *Tetrahedron Lett.*, 533 (1962).

(25) F. Minisci, R. Galli, M. Cecere, V. Malatesta, and T. Caronna, *Tetrahedron Lett.*, 5609 (1968); F. Minisci, M. Cecere, and R. Galli, *Chim. Ind. (Milan)*, 51, 385 (1969); F. Minisci, P. Zammori, R. Bernardi, M. Cecere, and R. Galli, *Tetrahedron*, 26, 4153 (1970); F. Minisci, *Synthesis*, 1 (1973).

The redox chain of Scheme IV finds explanation in the fact that the alkyl radical R·, because of its nucleophilic character, adds mainly to olefin **3**. The newly formed radical **4** has electrophilic character due to the proximity of the X group, and subsequent addition selectivity occurs on olefin **5**. Copolymerization or telomerization is completely prevented by quantitative oxidation of the allyl or benzyl radical **6**, whereas radical **4** is practically not oxidized because of its higher ionization potential and radical R· is oxidized only to a slight degree in the presence of olefin **3**. The selective oxidations of radicals R·, **4**, and **6** are strictly related to their relative nucleophilicities.

Reactions 31b and 31c[25] are typical examples of

$$(n\text{-}C_4H_9COO)_2 \; + \; CH_2{=}CHCN \; +$$

$$CH_2{=}CH{-}CH{=}CH_2 \xrightarrow[CH_3COOH]{Cu^+}$$

$$n\text{-}C_4H_9CH_2\underset{\underset{CN}{|}}{C}HCH_2\underset{\underset{OCOCH_3}{|}}{C}HCH{=}CH_2 \; +$$

$$n\text{-}C_4H_9CH_2\underset{\underset{CN}{|}}{C}HCH_2CH{=}CHCH_2OCOCH_3 \quad (31b)$$

$$68\%$$

$$+ \; H_2O_2 \; + \; CH_2{=}CHCOOH \; + \; CH_2{=}\underset{\underset{CH_3}{|}}{C}Ph \xrightarrow[CH_3OH]{Fe^{2+}-Cu^{2+}}$$

$$CH_3OOC(CH_2)_6\underset{\underset{CO{-}{-}{-}{-}O}{|}}{C}H{-}CH_2{-}\underset{\underset{CH_3}{|}}{\overset{Ph}{C}} \quad (31c)$$

$$55\% \text{ based on } H_2O_2$$
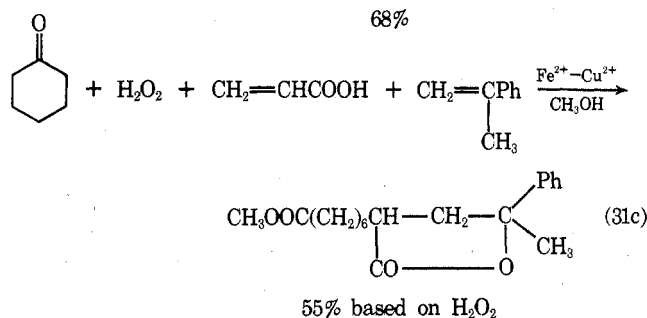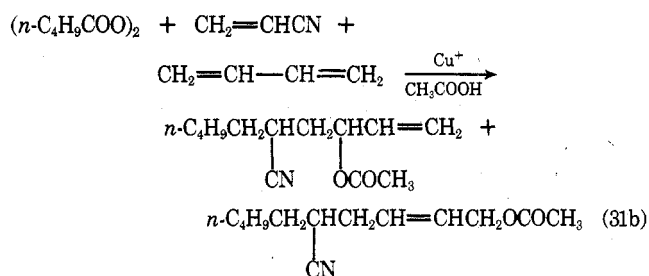
this general process. Addition of alkyl radicals according to process b, selective reaction with a metal salt, is shown by the Heiba reaction[26] of acetic acid or aliphatic ketones or aldehydes with olefins (Scheme V). The reaction has a close analogy with

Scheme V

$$CH_3COOH \; + \; Mn^{3+} \longrightarrow \; \cdot CH_2COOH \; + \; Mn^{2+} \; + \; H^+$$

$$HOOC\dot{C}H_2 \; + \; CH_2{=}CHC_6H_{13} \longrightarrow HOOCCH_2CH_2\dot{C}HC_6H_{13}$$

$$HOOCCH_2CH_2\dot{C}HC_6H_{13} \; + \; Mn^{3+} \longrightarrow$$

$$\underset{\underset{CO{-}{-}O}{|}}{\overset{CH_2{-}CH_2}{|}}{\diagdown}CHC_6H_{13} \; + \; Mn^{2+} \; + \; H^+$$

$$74\%$$
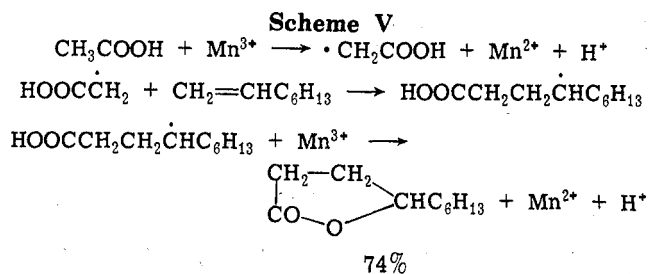
that of Scheme IV. The different polar character of the two radicals involved in Scheme V is of central significance. However, the reaction is not a chain process, and a stoichiometric amount of Mn^{3+} is required.

A more sophisticated synthesis related to Scheme V is shown by Scheme VI.[27]

In this non-chain redox process advantage is taken of the high reactivity of the nucleophilic alkyl radical **8** toward protonated heteroaromatic bases (ArH_2^+) such as the pyridinium ion, which successfully com-

Scheme VI

$$CH_3COCH_3 \; + \; Mn^{3+} \longrightarrow \; \cdot CH_2COCH_3 \; + \; Mn^{2+} \; + \; H^+$$
$$ \textbf{7}$$

$$CH_3COCH_2\cdot \; + \; \underset{|}{\overset{|}{C}}{=}\underset{|}{\overset{|}{C}} \longrightarrow CH_3COCH_2\underset{|}{\overset{|}{C}}{-}\underset{|}{\overset{|}{C}}\cdot$$
$$ \textbf{8}$$

$$CH_3COCH_2\underset{|}{\overset{|}{C}}{-}\underset{|}{\overset{|}{C}}\cdot \; + \; (ArH_2)^+ \longrightarrow CH_3COCH_2\underset{|}{\overset{|}{C}}{-}\underset{|}{\overset{|}{C}}ArH_2^{+}\cdot$$
$$ \textbf{9}$$

$$CH_3COCH_2\underset{|}{\overset{|}{C}}{-}\underset{|}{\overset{|}{C}}ArH_2^{+}\cdot \; + \; Mn^{3+} \longrightarrow$$

$$CH_3COCH_2\underset{|}{\overset{|}{C}}{-}\underset{|}{\overset{|}{C}}ArH^+ \; + \; H^+ \; + \; Mn^{2+}$$
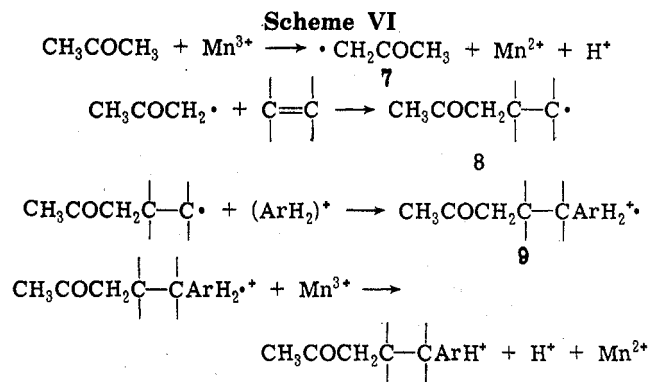
pete with the electron-transfer oxidation, and of the different oxidizability of radicals **7**, **8**, and **9**. Moreover, it is of synthetic interest that radical **7** does not attack ArH_2^+ and that aromatic substitution is highly selective.[28]

Process c is best exemplified by the addition of carbon free radicals R· to butadiene or other conjugated alkenes and dimerization of the relatively stable radical adducts. A large variety of carbon free radicals generated by redox systems react according to Scheme VII.[29]

Scheme VII

$$\text{redox system} \longrightarrow R\cdot$$

$$R\cdot \; + \; CH_2{=}CH{-}CH{=}CH_2 \longrightarrow$$

$$RCH_2\dot{C}HCH{=}CH_2 \longleftrightarrow RCH_2CH{=}CHCH_2\cdot$$

$$2RC_4H_6\cdot \diagup\!\!\!\begin{array}{l} RCH_2\underset{\underset{CH{=}CH_2}{|}}{C}H\underset{\underset{CH{=}CH_2}{|}}{C}HCH_2R \\[1.5em] RCH_2CH{=}CHCH_2CH_2CH{=}CHCH_2R \\[1em] R\underset{\underset{CH{=}CH_2}{|}}{C}HCH_2CH{=}CHCH_2R \end{array}$$
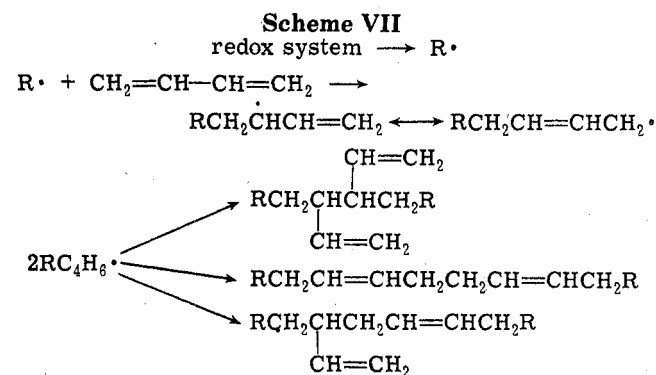
When the reaction sequence of Scheme IV was carried out in the presence of iron instead of copper salts, dimerization of the radical **6** (eq 32) was observed.[30]

$$2RCH_2CHXCH_2\dot{C}HY \rightarrow RCH_2CHXCH_2CHYCHYCH_2CHXCH_2R \tag{32}$$

Scheme VIII

$$H_2O_2(S_2O_8{}^{2-}) \; + \; Fe^{2+} \longrightarrow Fe^{3+} \; + \; \cdot OH(SO_4\cdot{}^-) \; + \; OH^-(SO_4{}^{2-})$$

$$HO\cdot (SO_4\cdot{}^-) \; + \; FeN_3{}^{2+} \longrightarrow N_3\cdot \; + \; Fe^{3+} \; + \; OH^-(SO_4{}^{2-})$$

$$N_3\cdot \; + \; \underset{|}{\overset{|}{C}}{=}\underset{|}{\overset{|}{C}} \longrightarrow N_3{-}\underset{|}{\overset{|}{C}}{-}\underset{|}{\overset{|}{C}}\cdot$$

$$N_3{-}\underset{|}{\overset{|}{C}}{-}\underset{|}{\overset{|}{C}}\cdot \; + \; FeN_3{}^{2+} \longrightarrow N_3\underset{|}{\overset{|}{C}}{-}\underset{|}{\overset{|}{C}}{-}N_3 \; + \; Fe^{2+}$$

$$N_3{-}\underset{|}{\overset{|}{C}}{-}\underset{|}{\overset{|}{C}}\cdot \; + \; FeCl^{2+} \longrightarrow N_3{-}\underset{|}{\overset{|}{C}}{-}\underset{|}{\overset{|}{C}}{-}Cl \; + \; Fe^{2+}$$
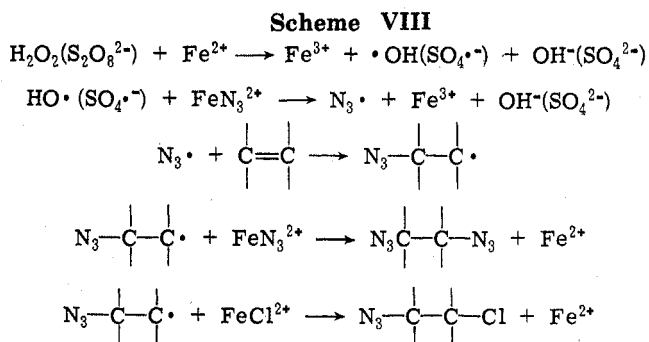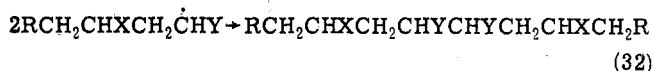
Nitrogen Free Radicals. Diazidation or chloroazidation of the double bond[24,31-33] (Scheme VIII) in-

(26) E. I. Heiba and R. M. Dessau, *J. Am. Chem. Soc.*, **93**, 524 (1971); **94**, 2888 (1972), and references quoted.

(27) F. Minisci, A. Moro, and O. Porta, unpublished results.

(28) F. Minisci and O. Porta, *Advan. Heterocycl. Chem.*, **16**, 123 (1974).

(29) G. Sosnovsky and D. J. Rawlinson, "Organic Peroxides", Vol. II, D. Swern, Ed., Wiley, New York, N.Y., 1971, p 152.

(30) F. Minisci, M. Cecere, R. Galli, and A. Selva, *Org. Prep. Proced.*, **1**, 11 (1969).

(31) F. Minisci and R. Galli, *Tetrahedron Lett.*, 355 (1963).

volves ligand-transfer redox chains that can be included in general process a. As the transfer of a chlorine atom to the radical adduct is faster than that of an azido group it is possible to obtain azidochlorination in the presence of $FeCl_3$. The lack of the stable pseudohalogen molecule N_6 makes impracticable a conventional chain addition and confers to the redox diazidation of olefins a considerable synthetic interest for the preparation of vicinal diamines. Diazidation of styrene (eq 33) and chloroazidation of cyclohexene (eq 34) emphasize the interest of the general process of Scheme VIII.

$$PhCH=CH_2 + 2NaN_3 \xrightarrow[Fe^{2+}]{(NH_4)_2S_2O_8} PhCH-CH_2 \qquad (33)$$
$$\underset{N_3}{|} \quad \underset{N_3}{|}$$

89% based on styrene

$$+ NaN_3 + FeCl_3 \xrightarrow[Fe^{2+}]{H_2O_2} \qquad (34)$$

80% based on cyclohexene

A redox chain aminochlorination and azidation of olefins have been accomplished with NH_2OSO_3H according to Scheme IX.[34,35] These reactions get

Scheme IX

$$^+NH_3OSO_3^- + Fe^{2+} \longrightarrow {}^+N\overset{\cdot}{H}_3 + Fe^{3+}$$

$$^+N\overset{\cdot}{H}_3 + \underset{|}{\overset{|}{C}}=\underset{|}{\overset{|}{C}} \longrightarrow {}^+NH_3-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}\cdot$$

$$^+NH_3-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}\cdot + FeX^{2+} \longrightarrow {}^+NH_3-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-X + Fe^{2+}$$

X = Cl, N_3

around the failure of the reaction when NH_2Cl is used in free-radical chain additions and also circumvent the nonavailability of NH_2N_3.

An analogous redox chain has been achieved by an electron-transfer oxidation of the radical adduct[34] (Scheme X). A non-chain redox addition (process b)

Scheme X

$$PhCH=CH_2 + \overset{+}{N}H_3 \longrightarrow Ph\overset{\cdot}{C}HCH_2\overset{+}{N}H_3$$

$$Ph\overset{\cdot}{C}HCH_2\overset{+}{N}H_3 + Fe^{3+} \longrightarrow Ph\overset{+}{C}HCH_2\overset{+}{N}H_3 + Fe^{2+}$$

$$Ph\overset{+}{C}HCH_2\overset{+}{N}H_3 + CH_3OH \longrightarrow Ph\underset{\underset{OCH_3}{|}}{C}HCH_2\overset{+}{N}H_3 + H^+$$

occurs in the synthesis of amine ketones,[13,36] outlined in Scheme XI.

Amino radicals generated in redox systems have also been added to butadiene and styrene with dimerization of the resulting allyl or benzyl radicals[13,37] (process c) as mentioned for carbon free radicals (Scheme XII).

Oxygen Radicals. Alkoxy radicals do not add to simple olefins, allylic hydrogen abstraction being the favored process, unless the electrophilic character is

Scheme XI

$$(n\text{-}C_4H_9)_2NCl + Fe^{2+} \longrightarrow (n\text{-}C_4H_9)_2\overset{\cdot}{N}\cdot + FeCl^{2+}$$

$$(n\text{-}C_4H_9)_2\overset{\cdot}{N}\cdot + CH_2=CHPh \longrightarrow (n\text{-}C_4H_9)_2NCH_2\overset{\cdot}{C}HPh$$

$$(n\text{-}C_4H_9)_2NCH_2\overset{\cdot}{C}HPh + O_2 \longrightarrow (n\text{-}C_4H_9)_2NCH_2\underset{\underset{O-O\cdot}{|}}{C}HPh$$

$$(n\text{-}C_4H_9)_2NCH_2\underset{\underset{O-O\cdot}{|}}{C}HPh + Fe^{2+} \longrightarrow$$

$$(n\text{-}C_4H_9)_2NCH_2COPh + Fe^{3+} + OH^-$$
$$76\%$$

Scheme XII

$$NH_2OH + Ti^{3+} \longrightarrow \cdot NH_2 + Ti^{4+}$$

$$\cdot NH_2 + CH_2=CH-CH=CH_2 \longrightarrow NH_2C_4H_6\cdot$$

$$2NH_2C_4H_6\cdot \longrightarrow NH_2C_4H_6C_4H_6NH_2$$

enhanced, as in $(CF_3)_3CO\cdot$.[38] They add to electron-rich conjugated olefins, such as butadiene and styrene, and redox chains were obtained by both ligand- and electron-transfer (process a)[24,39] (Scheme XIII).

Scheme XIII

$$(CH_3)_3COOH + Fe^{2+} \longrightarrow (CH_3)_3CO\cdot + Fe^{3+} + OH^-$$

$$(CH_3)_3CO\cdot + CH_2=CHCH=CH_2 \longrightarrow (CH_3)_3COC_4H_6\cdot$$

$$(CH_3)_3COC_4H_6\cdot + FeX^{2+} \longrightarrow (CH_3)_3COC_4H_6X + Fe^{2+}$$
$$X = \text{halogen, } N_3, \text{ SCN}$$

$$(CH_3)_3COC_4H_6\cdot + Cu^{2+} \longrightarrow (CH_3)_3COC_4H_6^+ + Cu^+$$

$$(CH_3)_3COC_4H_6^+ + ROH \longrightarrow (CH_3)_3COC_4H_6OR + H^+$$

It should be noted that under the same conditions acrylonitrile and *t*-BuOOH react mainly to add a methyl group and a halogen atom to the double bond.[24] Polar effects determine the course of the two reactions: acrylonitrile has a reduced reactivity toward the electrophilic *tert*-butoxy radical; as a result the *tert*-butoxy radical undergoes β scission to give acetone and the methyl radical (eq 28), which is nucleophilic and easily attacks acrylonitrile, producing ultimately α-halobutyronitrile.

A recent intramolecular non-chain redox addition

Scheme XIV

(32) F. Minisci, R. Galli, and M. Cecere, *Gazz. Chim. Ital.*, **94**, 67 (1964).
(33) R. Galli and V. Malatesta, *Org. Prep. Proced. Int.*, **3**, 227 (1971).
(34) F. Minisci and R. Galli, *Tetrahedron Lett.*, 1679 (1965).
(35) F. Minisci, R. Galli, and M. Cecere, *Chim. Ind.* (*Milan*), **48**, 132 (1966).
(36) F. Minisci and R. Galli, *Tetrahedron Lett.*, 3197 (1964).
(37) C. J. Albisetti, D. D. Cofmann, F. W. Hoover, E. L. Jenner, and W. E. Mochel, *J. Am. Chem. Soc.*, **81**, 1489 (1959).
(38) A. G. Davies, R. W. Dennis, B. P. Roberts, and R. C. Dobbie, *J. Chem. Soc., Chem. Commun.*, 468 (1974).
(39) J. K. Kochi, *J. Am. Chem. Soc.*, **84**, 2785 (1962).

of phenoxy radical to an olefinic bond (process b) is shown in Scheme XIV.[40]

The addition to butadiene of hydroxy and alkoxy radicals generated by redox systems can also lead to dimerization of the intermediate allyl radicals (process c), as mentioned for carbon and nitrogen radicals.[29]

(40) L. Merlini, unpublished results at Istituto di Chimica del Politecnico (Milan).

Conclusion

A better understanding of reduction–oxidation processes involving free radicals and of polar effects in free-radical reactions has contributed to intensification of both theoretical and synthetic interest in redox additions to olefins. Research in this field offers further possibilities of development, because it appears that a systematic investigation has not yet been carried out.

Solid-State Pressure Effects on Stereochemically Nonrigid Structures

John R. Ferraro*

Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439

Gary J. Long

Department of Chemistry, University of Missouri—Rolla, Rolla, Missouri 65401

The geometric structure of a molecule depends upon the magnitude of the energy barrier which prevents conversion into any of its geometric isomers.

In an extensive and impressive group of papers,[1,2] Pearson has presented a series of symmetry rules which may be used to predict the most stable structure of a molecule,[1] its structural rigidity, and its mode of reaction.[2] The rules, which are an extension of the work of Bader,[3] are based upon the use of perturbation theory and group theory to evaluate the effect of a vibrational distortion on the ground-state geometric configuration of a molecule. The theory supporting these symmetry rules has been extensively developed during the past few years.[1-4]

However, in general, experimental verification of the rules has been based upon molecular interconversions or reactions which occur either in solution or in the isolated gaseous state. The reliability of these orbital symmetry rules in predicting a stereochemically rigid or flexible geometric structure in the solid state has not as yet been experimentally confirmed.

This Account presents evidence which indicates that these symmetry rules are useful for predicting

solid-state structural interconversions between geometric isomers at high pressure. Due to space limitation, an extension of the ideas on this topic will be presented elsewhere.[5] Furthermore, this Account provides a new approach to the classification of the various effects which are observed in coordination compounds under high pressure.

In the approach developed by Pearson,[1] it is first assumed that all first-order structural distortions of the molecular geometry have occurred. These distortions include any first-order Jahn–Teller distortions required to produce a nondegenerate electronic ground state, and any vibrational distortions which can occur along the totally symmetric normal vibrational modes. On the basis of this assumption, the energy of an initial molecular configuration in the presence of a distortion may be expressed as

$$E = E_0 + \frac{1}{2}Q^2 \int \psi_0 \left| \frac{\partial^2 v}{\partial Q^2} \right| \psi_0 \mathrm{d}\tau + \sum_k \frac{\left[Q \int \psi_0 \left| \frac{\partial v}{\partial Q} \right| \psi_k \mathrm{d}\tau \right]^2}{E_0 - E_k} \tag{1}$$

$$E = E_0 + f_{00}Q^2 + f_{0k}Q^2 \tag{2}$$

where Q is a measure of the magnitude of the displacement of the initial molecular configuration along a normal coordinate which is then designated

John R. Ferraro received his B.S. and Ph.D. at Illinois Institute of Technology, and his M.S. at Northwestern University. He has been at Argonne National Laboratory since 1948, and is presently a senior chemist. His research interests are in the area of molecular spectroscopy of inorganic and coordination complexes.

Gary J. Long, who is an Associate Professor of Chemistry at the University of Missouri—Rolla, was born in Binghamton, N.Y., in 1941. He received his B.S. degree from Carnegie-Mellon University and his Ph.D. with Professor W. A. Baker, Jr., from Syracuse University where he was an NIH Doctoral Research Fellow. His research has dealt mainly with investigation of the magnetic, electronic, and structural properties of transition-metal complexes. During the 1974–1975 academic year Dr. Long is on sabbatical leave at the Inorganic Chemistry Laboratory at Oxford University in England.

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