Free-Radical Rearrangements in Telomerization

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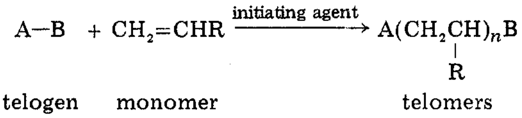
Since the 1940s, when the first reports on free-radical telomerization appeared,[1] this field of study has been fast developing. Formally, telomerization can be described by



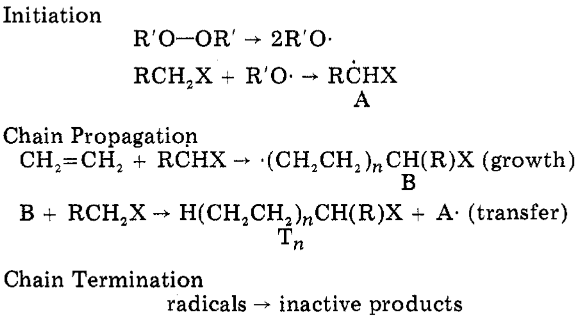
$$\underset{\text{telogen}}{\text{A–B}} + \underset{\text{monomer}}{CH_2{=}CHR} \xrightarrow{\text{initiating agent}} \underset{\text{telomers}}{A(CH_2\underset{R}{C}H)_nB}$$

Three aspects of telomerization are of interest to chemists. Of primary importance is the synthetic potential of the reaction as a unique one-step route to mono-, di-, and polyfunctional compounds. In addition, studies of telomerization offer a new approach to some general problems of radical chemistry, providing insight into the patterns and mechanisms governing substitution, fragmentation, and isomerization of radicals as well as factors determining their stability and reactivity. Yet another area of interest is the use of the reaction as a model process for solving certain problems of polymer chemistry. A sizable literature of articles and patents, together with a comprehensive monograph[1] and a number of review papers,[2,3] reflect the importance ascribed to these problems in current chemistry.

Any olefinic compound that can polymerize by the radical mechanism can, in principle, play the part of a monomer in telomerization. Although new telogens are reported from time to time, their number remains rather limited because only compounds containing bonds that readily undergo homolytic cleavage can act as telogens. Oxygen-containing species which react via cleavage of a C–H bond make up an important class of telogens. These include alcohols, ethers, acetals, ketones, carboxylic acids, and their derivatives. Interest of researchers in telogens of this type stems from their diversity and accessibility, as well as from their potential as starting materials for synthesis of many valuable products having not only synthetic but also industrial applicability. Telomerization with oxygen-containing agents proceeds as shown in Scheme I for ethylene. Scheme I ignores all the accompanying, side, and secondary reactions that may be involved in telomerization. In most cases, RO· radicals react by abstraction of hydrogen from the α-carbon atom.

Scheme I

Telomerization Mechamism[a]



Initiation

$$R'O\text{–}OR' \rightarrow 2R'O\cdot$$

$$RCH_2X + R'O\cdot \rightarrow \underset{A}{R\dot{C}HX}$$

Chain Propagation

$$CH_2{=}CH_2 + R\dot{C}HX \rightarrow \underset{B}{\cdot(CH_2CH_2)_nCH(R)X} \text{ (growth)}$$

$$B + RCH_2X \rightarrow \underset{T_n}{H(CH_2CH_2)_nCH(R)X} + A\cdot \text{ (transfer)}$$

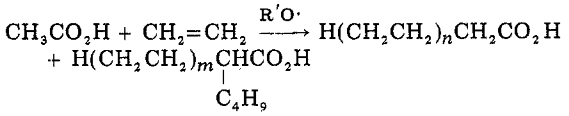
Chain Termination

$$\text{radicals} \rightarrow \text{inactive products}$$

[a] X is OH, COOR'', CN, etc. R is any substituent, n is 1, 2, 3. . . T_n are telomers containing n monomer units in the chain.

Scheme II

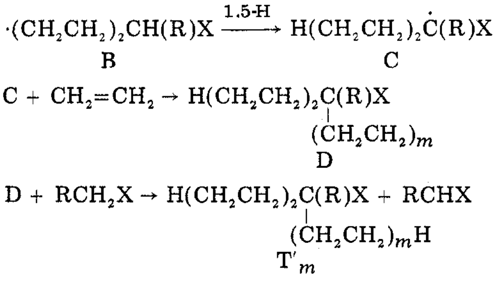
Telomerization of Ethylene with Acetic Acid



$$CH_3CO_2H + CH_2{=}CH_2 \xrightarrow{R'O\cdot} H(CH_2CH_2)_nCH_2CO_2H + H(CH_2CH_2)_m\underset{C_4H_9}{C}HCO_2H$$

Scheme III[a]

1,5 Hydrogen Shift in Growing Radicals



$$\underset{B}{\cdot(CH_2CH_2)_2CH(R)X} \xrightarrow{1.5\text{-H}} \underset{C}{H(CH_2CH_2)_2\dot{C}(R)X}$$

$$C + CH_2{=}CH_2 \rightarrow H(CH_2CH_2)_2\underset{\underset{D}{(\dot{C}H_2CH_2)_m}}{C}(R)X$$

$$D + RCH_2X \rightarrow \underset{T'_m}{H(CH_2CH_2)_2\underset{(CH_2CH_2)_mH}{C}(R)X} + R\dot{C}HX$$

[a] For notation, see Scheme I.

It was first discovered in 1964, in studies of telomerization of ethylene with acetic acid[4] and cyclohexane,[5] that isomerization of growing radicals via 1,5-hydrogen shift may occur during the reaction and may lead to formation of two series of telomers (Scheme II). Later, isomerization was shown to be typical of telomerizations proceeding by cleavage of telogen C–H bonds. It thus proved necessary to improve that part of Scheme I which describes development of the chain process by the addition of new steps accounting for formation of rearrangement radicals and their participation in chain propagation and chain transfer (Scheme III). Thus, in addition to "normal" telomers (T_n), products from rearrangement radicals (T'_m) are generated. Depending on the number of carbon atoms separating the radical

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(1) Ch. Starks, "Free-Radical Telomerization", Academic Press, New York, N.Y., 1974.

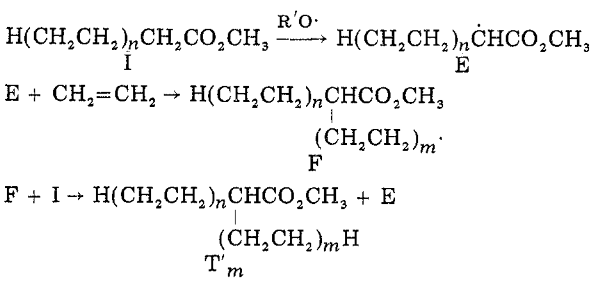
(2) R. Kh. Freidlina, E. I. Vasil'eva, E. Ts. Chukovskaya, and B. A. Englin, *Usp. Khim. Polim.*, 138 (1966).

(3) F. Minisci, *Acc. Chem. Res.*, **8**, 165 (1975).

(4) R. Kh. Freidlina, S. N. Aminov, and A. B. Terent'ev, *Dokl. Akad. Nauk SSSR*, **156**, 1133 (1964).

(5) C. Huggett, T. R. Walton, C. R. Midkiff, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **5**, 106 (1964).

Scheme IV
Secondary Telomerization



$$\underset{\mathrm{I}}{\mathrm{H(CH_2CH_2)_{\mathit{n}}CH_2CO_2CH_3}} \xrightarrow{\mathrm{R'O\cdot}} \underset{\mathrm{E}}{\mathrm{H(CH_2CH_2)_{\mathit{n}}\dot{C}HCO_2CH_3}}$$

$$\mathrm{E + CH_2{=}CH_2 \rightarrow} \underset{\mathrm{F}}{\mathrm{H(CH_2CH_2)_{\mathit{n}}CHCO_2CH_3(CH_2CH_2)_{\mathit{m}}\cdot}}$$

$$\mathrm{F + I \rightarrow} \underset{\mathrm{T'_{\mathit{m}}}}{\mathrm{H(CH_2CH_2)_{\mathit{n}}CHCO_2CH_3(CH_2CH_2)_{\mathit{m}}H}} + \mathrm{E}$$

center and the carbon atom from which hydrogen is abstracted, various types of isomerization are referred to as 1,3, 1,4, 1,5, etc., radical shifts.[6]

Studies of reactions involving intramolecular hydrogen abstraction furnish valuable information about various aspects of radical rearrangement processes in the liquid phase. Thus, telomerization of ethylene and propylene with acetic and propionic acids and their derivatives provides strictly identical conditions for comparison of the 1,3- and 1,5-hydrogen shifts. Likewise, comparison of the 1,4 and 1,6 shifts can be made by using the data on telomerization of ethylene with methyl formate.

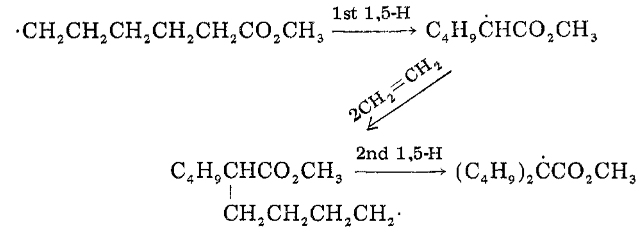
The principal difficulty one encounters in treatment of telomerization reactions involving two series of telomers arises from the fact that the products of the T'_m series may originate not only from isomerization of radicals (Scheme III) but also from "secondary" telomerization according to Scheme IV. Apart from being of purely theoretical interest, knowledge of the mechanism governing the formation of T'_m isomers is essential for proper choice of experimental conditions favoring production of either "normal" (T_n) or rearrangement (T'_m) telomers, because only rearrangement can be responsible for selective formation of a single branched telomer series.

Most known telomerization reactions involving radical rearrangements proceed via intramolecular abstraction of hydrogen from position 5, relative to the radical center of a growing chain (1,5 shift). Few cases of 1,5-halo transfer, as well as of 1,6- or 1,3-hydrogen shift, have been reported. In our discussion of various types of rearrangements, we shall proceed from those encountered most frequently to less common ones.

Radical Rearrangements Involving 1,5 Shifts

Monocarboxylic Acids and Their Derivatives as Telogens. Experiments on telomerization of ethylene with acetic acid resolve the question of what combination of features may serve to distinguish between radical rearrangement and secondary telomerization mechanisms for formation of certain branched telomers. Acetic acid and its derivatives (methyl acetate, acetonitrile) can be expected to telomerize ethylene to a number of telomers of normal structure in the presence of radical initiating agents. A detailed study of the product mixture, however, showed it to contain α-ethyl- and α-butylcaproic acids as well as nonbranched telomers T_n, $n = 1$–4 (butyric, caproic, caprylic, and capric acids)[4,7,8] (see Scheme II).

Scheme V
Repeated Rearrangement



$$\cdot\mathrm{CH_2CH_2CH_2CH_2CH_2CO_2CH_3} \xrightarrow{\text{1st 1,5-H}} \mathrm{C_4H_9\dot{C}HCO_2CH_3}$$

$$\xrightarrow{\mathrm{2CH_2{=}CH_2}}$$

$$\underset{\mathrm{CH_2CH_2CH_2CH_2\cdot}}{\mathrm{C_4H_9CHCO_2CH_3}} \xrightarrow{\text{2nd 1,5-H}} \mathrm{(C_4H_9)_2\dot{C}CO_2CH_3}$$

The radical rearrangement origin of the branched products can be recognized from the following considerations.

(a) Acetic acid and its derivatives are exceedingly poor telogens for ethylene. Their conversions do not exceed 1–3% so that T_n telomers occur in the reaction mixture in very small concentrations (below 0.5%). This predicts low probabilities for secondary reactions.

(b) α-Ethyl- and α-butylcaproic acids are formed in yields well above that of caproic acid. This would be compatible with the secondary telomerization mechanism in case of high conversions of the latter. Independent experiments with pure caproic acid, however, give conversions not exceeding 3.5% under comparable conditions.

(c) The reaction mixture does not contain α-ethylbutyric acid in any appreciable amount. This product would occur if secondary reaction of butyric acid (T_1) with ethylene took place. Independent experiments have demonstrated that butyric and caproic acids are of comparable reactivity.

(d) Relative kinetics of the reaction have been studied to show that chain-transfer coefficients vary nonmonotonicaly with n. This is unlike the situation when no radical rearrangement is involved (see below).

It thus follows that the formation of α-ethyl- and α-butylcaproic acids in the reaction under discussion proceeds via 1,5-hydrogen shift in the $\cdot\mathrm{CH_2CH_2CH_2CH_2CH_2CO_2H}$ radical, according to Scheme III. It can also be stated that no 1,3-hydrogen shift in the $\cdot\mathrm{CH_2CH_2CH_2CO_2H}$ radical occurs. Such rearrangement would lead to the formation of α-ethylbutyric acid, which is absent from the reaction products. Radicals of normal structure are known to undergo 1,5 intramolecular hydrogen abstraction more readily than 1,3 abstraction.[6]

Telomerizations with acetic acid and its derivatives of the general formula $\mathrm{CH_3X}$ are remarkable in that they may involve repeated rearrangement of radicals. The only reaction of this type studied in detail is that of ethylene with methyl acetate.[9] Along with telomers $\mathrm{H(CH_2CH_2)_{\mathit{n}}CH_2CO_2CH_3}$ (T_n, $n = 1$–6), $\mathrm{H(CH_2CH_2)_{\mathit{m}}CH(C_4H_9)CO_2CH_3}$ (T'_m, $m = 1$–3), and the products from hydrogen abstraction from the methoxyl group, $\mathrm{CH_3COOCH_2(CH_2CH_2)_{\mathit{n}}H}$ (T^e_n, $n = 1$–3), the reaction gives repeated rearrangement telomers, $\mathrm{H(CH_2CH_2)_{\mathit{p}}C(C_4H_9)_2CO_2CH_3}$ (T''_p, $p = 1, 2$) (Scheme V).

Recently, the Japanese authors[10] have also studied telomerization of ethylene with methyl acetate and identified T_n ($n = 1$–7), T'_m ($m = 1$–5), and T^e_n ($n = 1$–7) telomers, as well as telomers CH$_3$COOCH-

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(6) R. Kh. Freidlina, *Adv. Free-Radical Chem.*, 1, 211 (1965).

(7) S. N. Aminov, A. B. Terent'ev, and R. Kh. Freidlina, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1855 (1965).

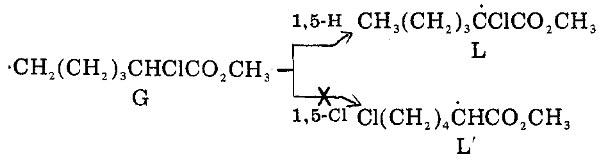
(8) Y. Suhara, *Bull. Chem. Soc. Jpn.*, 46, 990 (1973).

(9) N. S. Ikonnikov, A. B. Terent'ev, M. A. Churilova, and R. Kh. Freidlina, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2479 (1972).

(10) T. Fujimoto and J. Hirao, *Bull. Chem. Soc. Jpn.*, 47, 1930 (1974).

Scheme VI

Radical Rearrangements in Telomerization of Ethylene with Methyl Chloroacetate



$(C_4H_9)(CH_2CH_2)_nH$ (n = 1–3). The latter products originate from 1,5-hydrogen shifts in $CH_3COOCH_2(CH_2CH_2)_2\cdot$ radicals. One of the earliest patents for telomerization of ethylene with acetic acid[11] also stresses the very complicated nature of the process. Telomerizations of ethylene[7,12] and tetrafluoroethylene[13] with acetonitrile follow similar patterns to those discussed above.

Methyl monochloro- and monobromoacetates behave quite differently in telomerization of ethylene. These reactions clearly demonstrate that development of the process and extent of rearrangement depend strongly on the nature of the bond undergoing cleavage and on the reactivity of telogens in chain transfer. Abstraction of bromine occurs in the case of methyl monobromoacetate. With this telogen, the rate of chain transfer exceeds those of chain propagation and of isomerization of intermediate radicals. As a result, nonbranched lower telomers $Br(CH_2CH_2)_nCH_2COOCH_3$ (T_n, n = 1–3) are the major products observed under usual conditions.[9] In contrast, methyl chloroacetate reacts almost exclusively by hydrogen abstraction;[14,15] the introduction of chlorine as substituent in methyl acetate considerably enhances its telogen reactivity. The product mixture from telomerization of ethylene with methyl monochloroacetate contains nonbranched telomers $H(CH_2CH_2)_nCHClCOOCH_3$ (T_n, n = 1–5) along with rearrangement telomers $H(CH_2CH_2)_m{-}C(C_4H_9)ClCOOCH_3$ (T'_m, m = 1, 2). Scheme VI, which includes rearrangement radicals formed by 1,5-hydrogen shift, offers a plausible explanation of these observations. The higher proportion of branched products in this reaction compared with that observed in telomerization with methyl acetate is due to the greater difference in stabilities of initial (G) and rearrangement (L) radicals; higher stability of L compared with L′, a possible product of 1.5-halo shift, may account for intramolecular abstraction of hydrogen rather than chlorine. Enhancement of radical stability caused by the presence of chloro substituents at the radical center is a well-known phenomenon.[6]

A number of homologues of acetic acid and their derivatives of the general formula RCH_2X (where R stands for CH_3, C_2H_5, C_4H_9, and X is CO_2H, CO_2CH_3, CN) merit interest because of their higher telogen reactivity toward ethylene, compared with parent compounds. This is mainly due to the fact that methylene groups undergo hydrogen abstraction more readily than methyl groups. Telomerizations with all telogens of this type involve 1,5 radical rearrangements.

In addition to proton NMR, GLC, and other techniques, carbon-13 NMR spectra were used for structure assignment of individual telomerization products.[12,16]

Difunctional Compounds as Telogens. Very few reactions of this type have been reported. The difunctional compounds studied include diethyl malonate,[17] acetoacetate,[18] methyl cyanoacetate,[10] dimethyl succinate, and dimethyl adipinate.[19] The first three compounds differ from those discussed above by the presence of reactive methylene groups CH_2XY (X and Y stand for $COOCH_3$, $COOC_2H_5$, CN, CH_3CO–) which enhance chain-transfer rates and lead to predominant formation of lower telomers.

Diethyl malonate reacts with ethylene to give $H(CH_2CH_2)_nCH(COOC_2H_5)_2$ (n = 1–3) and $R_1R_2C(COOC_2H_5)_2$ (where R_1 and R_2 stand for ethyl or butyl). Mechanistic interpretation of these results is not unambiguous because high reactivity of the C–H bonds in products $H(CH_2CH_2)_nCHXY$ requires that, together with rearrangement, secondary telomerization be taken into account as possible origin of dialkyl-substituted telomers. This statement finds experimental verification in the fact that telomerization of ethylene with malonates, acetoacetates, and cyanoacetates yields appreciable amounts of diethyl-substituted telomers having no analogues among the products from telomerization of ethylene with, e.g., acetic acid. One cannot also rule out the possibility of 1,3-hydrogen shift in radicals$\cdot CH_2CH_2CHXY$. The Japanese authors[10] suggest that the "normal" telomer radicals that occur in telomerization of ethylene with methyl cyanoacetate undergo 1,5-hydrogen shift, and all the "normal" products reenter the reaction as "secondary" telogens.

Other Compounds as Telogens. Radical rearrangements with 1,5-hydrogen shift were also observed in telomerizations of ethylene with hydrocarbons,[5,20] alcohols,[21-24] acetone,[25] and acetaldehyde.[26] Cyclohexane[5] reacts with ethylene to give mainly n-alkylcyclohexanes and 1-butyl-1-ethylcyclohexane. The latter is believed to originate from rearrangements of intermediate radicals. It should be noted that telomerization with hydrocarbons is a very complicated process leading to formation of a number of series of hydrocarbons. Lack of selectivity in these reactions leads one to suspect the occurrence of both rearrangement and side processes.

(11) F. W. Banes, W. P. Fitzgerald, and J. F. Nelson, U.S. Patent 2 585 723 (1952).

(12) A. B. Terent'ev, M. A. Churilova, V. I. Dostovalova, and V. A. Svoren', *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1814 (1974).

(13) L. Moore, private communication.

(14) M. S. Kharasch, W. H. Urry, and E. V. Jensen, *J. Am. Chem. Soc.*, **67**, 1626 (1945).

(15) R. Kh. Freidlina, A. B. Terent'ev, and N. S. Ikonnikov, *Dokl. Akad. Nauk SSSR*, **193**, 605 (1970).

(16) R. Kh. Freidlina, A. B. Terent'ev, and V. I. Dostovalova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2125 (1972).

(17) A. B. Terent'ev, S. N. Aminov, and R. Kh. Freidlina, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2042 (1965).

(18) A. B. Terent'ev, Yu. P. Chizhov, and P. Brakhme, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 176 (1970).

(19) A. B. Terent'ev and R. Kh. Freidlina, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1527 (1973).

(20) V. Jaacks and F. R. Mayo, *J. Am. Chem. Soc.*, **87**, 3371 (1965).

(21) M. Takehisa, M. Jasumoto, and J. Hosaka, *J. Chem. Soc. Jpn., Ind. Chem. Sect.*, **68**, 654 (1965).

(22) R. Kh. Freidlina, A. B. Terent'ev, M. Ya. Khorlina, and S. N. Aminov, *Zh. Vses. Khim. Ova.*, **11**, 211 (1966).

(23) R. A. Basson and L. V. Wyk, *J. Chem. Soc. B*, 809 (1971).

(24) P. A. Zagorets, A. G. Shostenko, and A. M. Dodonov, *Khim. Vys. Energ.*, **6**, 378 (1972).

(25) M. Ya. Khorlina and R. Kh. Freidlina, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 933 (1967).

(26) M. G. Vinogradov, G. I. Nikishin, A. B. Terent'ev, et al., Auth. Certificate 459455 (1972); *Bullet izobretenij*, No. 5 (1975).

In contrast, carbon tetrachloride, which is highly active in chain transfer, reacts with ethylene without any complications under normal conditions. In the gas phase, however, the reaction gives 1-hexene and tetrachloroheptane $CCl_3CH_2CHClCH_2CH_2CH_2CH_3$ along with tetrachloroalkanes $CCl_3(CH_2CH_2)_nCl$. The authors[20] explain the formation of the first two compounds as resulting from a number of transformations involving 1,5-hydrogen shift.

Telomerization of olefins with primary alcohols is, in principle, of considerable commercial interest.[27] Exceedingly complex product mixtures are, however, observed in these reactions. Telomerization of ethylene with methyl alcohol in the presence of peroxides or under ^{60}Co irradiation has been studied by a number of authors.[21-23] Lighter fractions of the reaction mixture contain the following primary and secondary alcohols: 1-propanol, 1-pentanol, 1-heptanol, 1-nonanol, 3-heptanol, 3-nonanol, and 5-nonanol. The authors[21] consider secondary alcohols as products from secondary telomerization with first-formed primary ones. In our view, the absence of 3-pentanol from the product mixture contradicts this interpretation. This alcohol should occur in telomerization of ethylene with 1-propanol, which has a comparable reactivity to that of 1-pentanol. Apart from that, it is noteworthy that the reaction gives secondary alcohols in high yields while conversion of methanol is low (less than 5%). These observations have driven us to the conclusion[22] that telomerizations with primary alcohols also involve 1,5-hydrogen shifts (see Scheme III, X = OH). More recently, telomerizations of ethylene with ethanol[23] and alcohols C_1–C_5,[24] and of trifluorochloroethylene with methanol[28] and ethanol[29] have been studied. The authors of these works share our point of view. Of course, with more reactive C_2–C_5 alcohols, secondary telomerization may contribute to the process.[1]

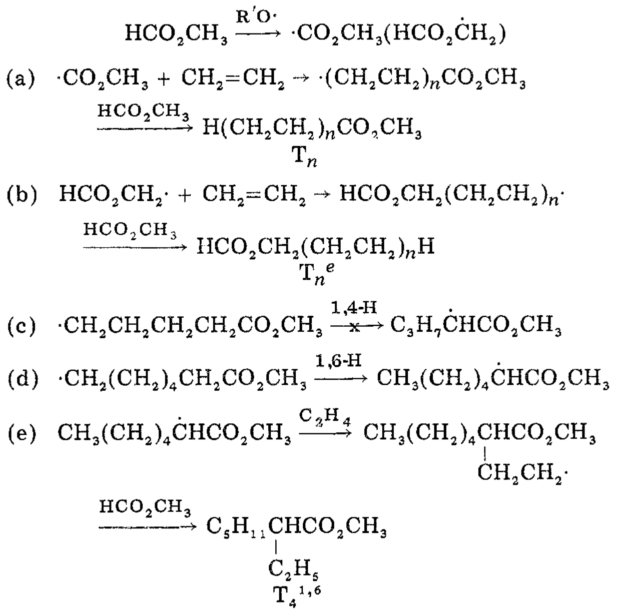
Radical Rearrangements Involving 1,4- and 1,6-Hydrogen Shifts

Interest of chemists in radical reactions of alkyl formates stems from the peculiar nature of the acyl C–H bond and from the fact that C–H bonds in both acyl and alkyl moieties may undergo cleavage, as detected by ESR[30] and isotopic effect[31] evidence.

Telomerization of ethylene with methyl formate is especially interesting because it provides possibilities for both 1,4- and 1,6-hydrogen shifts, as shown in Scheme VII. The product from 1,6 intramolecular hydrogen abstraction, methyl α-ethylhaptanoate (Scheme VII, e), is produced together with normal telomers T_n (n = 1–3) and T^e_n (n = 1–3) in telomerizations initiated by peroxides of γ irradiation.[32,33] The absence of methyl α-ethylvalerate from the product mixture shows that 1,4-hydrogen shift does not occur under telomerization conditions. It is noteworthy that the extent to which 1,6 rearrangement occurs is markedly lower compared with 1,5 rearrangement in all cases where such comparison can be drawn.

Scheme VII

Telomerization of Ethylene with Methyl Formate



$$HCO_2CH_3 \xrightarrow{R'O\cdot} \cdot CO_2CH_3(HCO_2\dot{C}H_2)$$

$$\text{(a)}\quad \cdot CO_2CH_3 + CH_2{=}CH_2 \rightarrow \cdot(CH_2CH_2)_nCO_2CH_3 \xrightarrow{HCO_2CH_3} \underset{T_n}{H(CH_2CH_2)_nCO_2CH_3}$$

$$\text{(b)}\quad HCO_2CH_2\cdot + CH_2{=}CH_2 \rightarrow HCO_2CH_2(CH_2CH_2)_n\cdot \xrightarrow{HCO_2CH_3} \underset{T_n{}^e}{HCO_2CH_2(CH_2CH_2)_nH}$$

$$\text{(c)}\quad \cdot CH_2CH_2CH_2CH_2CO_2CH_3 \xrightarrow[\times]{1,4\text{-H}} C_3H_7\dot{C}HCO_2CH_3$$

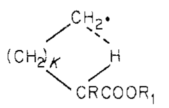
$$\text{(d)}\quad \cdot CH_2(CH_2)_4CH_2CO_2CH_3 \xrightarrow{1,6\text{-H}} CH_3(CH_2)_4\dot{C}HCO_2CH_3$$

$$\text{(e)}\quad CH_3(CH_2)_4\dot{C}HCO_2CH_3 \xrightarrow{C_2H_4} CH_3(CH_2)_4\underset{\substack{|\\CH_2CH_2\cdot}}{C}HCO_2CH_3 \xrightarrow{HCO_2CH_3} \underset{T_4{}^{1,6}}{C_5H_{11}\underset{\substack{|\\C_2H_5}}{C}HCO_2CH_3}$$

The predominance of telomers containing two monomer subunits per molecule in γ-irradiation-induced telomerization of ethylene with oxalyl chloride[34] is believed to be due to 1,6 intramolecular abstraction of chlorine.

The data on telomerization of ethylene show that radical rearrangements are typical of reactions of poor telogens. In most cases, 1,5-hydrogen shift occurs. 1,6 intramolecular hydrogen abstraction is less frequent, while 1,3 and 1,4 shifts have not been reported so far.

1,5 shifts in growing radicals are favored by a number of factors, two of which are worth mentioning here. First, the six-membered transition state involved in 1,5 intramolecular abstraction of hydrogen (**1**, k = 3) must have the lowest energy compared with those involved in other types of rearrangement. The second important factor is the polarity ratio of the radical center and functional groups in growing radicals. Thus, the fact that the radical center is a stronger electrophile in radicals with k of 1 and 2 than in those with k of 3 and 4 (**1**) hinders its attack on the $-CHRCOOR_1$ electrophile in the shorter radicals.



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At least three competing reactions of growing radicals should be taken into consideration. These are rearrangement, chain growth, and chain transfer. Significance of contributions from rearrangement depends on a number of factors determining relative rates of competing processes.

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(27) E. R. Gilliland and R. J. Kallal, *Chem. Eng. Progr.*, **49**, 647 (1953).

(28) F. Liska and S. Simek, *Collection Czech. Chem. Commun.*, **35**, 1752 (1970).

(29) F. Liska, V. Declek, and B. Chutny, *Collection Czech. Chem. Commun.*, **33**, 1299 (1968).

(30) P. Smith, J. Pearson, P. B. Wood, and T. Smith, *J. Chem. Phys.*, **43**, 1535 (1965).

(31) N. L. Arthur and P. Gray, *Trans. Farad. Soc.*, **65**, 424 (1969).

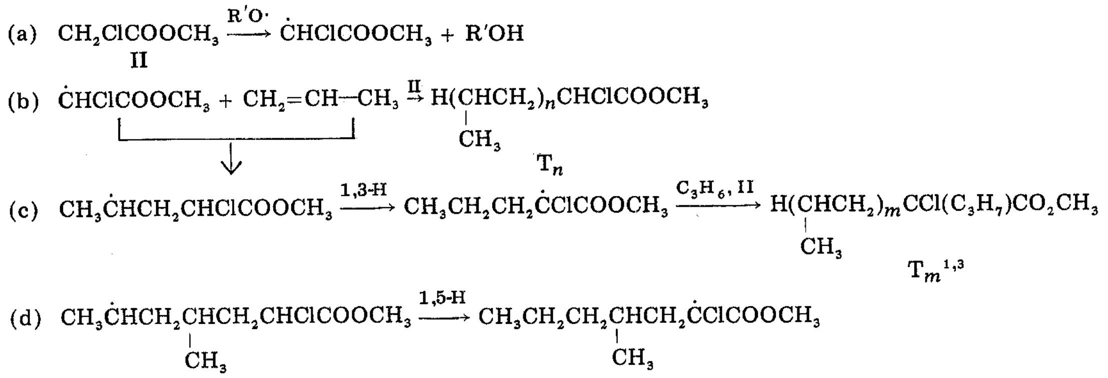
(32) I. N. Bryantsev, P. A. Zagorets, N. N. Romina, A. B. Terent'ev, and R. Kh. Freidlina, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 169 (1970).

(33) P. A. Zagorets, I. N. Bryantsev, and A. B. Terent'ev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 909 (1976).

(34) D. R. Napier, *J. Org. Chem.*, **30**, 1305 (1965).

Scheme VIII

Telomerization of Propylene with Methyl Chloroacetate



(a) $\underset{\textbf{II}}{CH_2ClCOOCH_3} \xrightarrow{R'O\cdot} \dot{C}HClCOOCH_3 + R'OH$

(b) $\dot{C}HClCOOCH_3 + CH_2{=}CH{-}CH_3 \xrightarrow{\textbf{II}} H(\underset{CH_3}{CH}CH_2)_nCHClCOOCH_3$ $\quad T_n$

(c) $CH_3\dot{C}HCH_2CHClCOOCH_3 \xrightarrow{1,3\text{-}H} CH_3CH_2CH_2\dot{C}ClCOOCH_3 \xrightarrow{C_3H_6,\ \textbf{II}} H(\underset{CH_3}{CH}CH_2)_mCCl(C_3H_7)CO_2CH_3$ $\quad T_m{}^{1,3}$

(d) $CH_3\dot{C}HCH_2\underset{CH_3}{CH}CH_2CHClCOOCH_3 \xrightarrow{1,5\text{-}H} CH_3CH_2CH_2\underset{CH_3}{CH}CH_2\dot{C}ClCOOCH_3$

Radical Rearrangements Involving 1,3 Hydrogen Shifts

Few examples of radical rearrangements involving 1,3 hydrogen shifts are known to occur in solution. Such processes are believed to be rare even in the gas phase.[35-39]

We have shown that 1,3 intramolecular hydrogen abstraction contributes substantially to telomerizations of propylene with methyl chloroacetate[40] and methyl propionate.[41] The first reaction yields telomers T_n (n = 1, 2) and $T_m{}^{1,3}$ (m = 1, 2) (Scheme VIII). Structure assignments of the reaction products are based on the proton and ^{13}C NMR data.[40] It has also been shown that, in addition to 1,3-hydrogen shifts in the radical containing one monomer unit, 1,5 shifts in the two-unit radical occur[42] (Scheme VIII, d).

Thus, the use of propylene as a monomer instead of ethylene gives essentially new results. The presence of an electron-releasing substituent (CH_3) at the radical center together with an electron-withdrawing one (Cl) in the α position facilitates 1,3-hydrogen shifts to the extent that the corresponding rearrangement products are formed in high yield. As mentioned, 1,3 shifts occur along with 1,5 shifts in this reaction. We believe that the polarity characteristics of the $CH_3\dot{C}HCH_2CHClCO_2CH_3$ radical which favor intramolecular chain transfer by the attack of the radical center nucleophile $CH_3\dot{C}H-$ on the $-CHClCO_2CH_3$ electrophile are responsible for the occurrence of 1,3-hydrogen shifts in the case of propylene.

Relative Kinetics of Telomerization Involving Radical Rearrangements

The principal steps involved in the propagation sequence, including radical rearrangement, are shown in Scheme IX.

Scheme IX

Chain Propagation in Telomerization[a]

(a) $R\dot{C}HX + CH_2{=}CH_2 \xrightarrow{K_g} \cdot(CH_2CH_2)_nCHRX$

(b) $\cdot(CH_2CH_2)_nCHRX + RCH_2X \xrightarrow{K_{tr}} H(CH_2CH_2)_nCHRX + R\dot{C}HX$

(c) $\underset{N'}{\cdot CH_2CH_2CH_2CH_2CHRX} \xrightarrow{K_i} \underset{N'}{CH_3CH_2CH_2CH_2\dot{C}RX}$

[a] K_g, K_{tr}, and K_i are rate constants of chain growth, chain transfer, and radical isomerization reactions, respectively.

Kinetics of telomerization are usually described in terms of partial chain-transfer coefficients, $C_n = K_{tr_n}/K_{g_n}$, which characterize relative reactivity of the radical containing n monomer units in chain-growth and chain-transfer reactions.[2,43] While C_n values provide quantitative information about relative contributions from chain-growth and -transfer processes, relative isomerization constants $C_i = K_i/K_g$ (mol/l.) give ratios of isomerization to chain-growth rate constants.[5] The partial constants are calculated according to the equations

$$C_n = (M/S)(T_n/\sum_{j>n} T_j)$$[43]

and

$$C_i = [M](\sum_{m\geqslant 1} T'_m/\sum_{n>2} T_n)$$

where M and S are molar concentrations of monomer and telogen, respectively, and T_n, T_j, and T'_m are molar fractions of respective telomers.

In addition, we have calculated formal constants $C_n{}^{\mathrm{sum}}$ by substituting into the equation for C_n[43] summary molar fractions of both "normal" and rearrangement telomers containing the same number of monomer units: T_1, T_2, $(T_3 + T'_1)$, $(T_4 + T'_2)$, etc.

In Table I, the data are presented for the "normal" (C_n), rearrangement (C'_m), and "summary" ($C_n{}^{\mathrm{sum}}$) series. One can see that the C_n and C'_m values increase smoothly in passing from n = 1 to n = 3. Further chain elongation has a negligible effect on C_n. The behavior of $C_n{}^{\mathrm{sum}}$ with variation of n depends on the reaction pattern. With reactions involving 1,5-hydrogen shifts, the minimum value of $C_n{}^{\mathrm{sum}}$ corresponds to the n = 2 radical, the radical which undergoes intramolecular

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(35) Yu. G. Bundel' and O. A. Reutov, *Dokl. Akad. Nauk SSSR*, **159**, 588 (1964).

(36) R. L. Huang, H. H. Lee, and L. Wong, *J. Chem. Soc.*, 6730 (1965).

(37) A. D. Stepukhovich and V. I. Babayan, *Usp. Khim.*, **41**, 1610 (1972).

(38) D. S. Tardy, *Int. J. Chem. Kinet.*, **6**, 291 (1974).

(39) E. A. Hardwidge, C. W. Larson, and B. S. Rabinovitch, *J. Am. Chem. Soc.*, **92**, 3278 (1970).

(40) A. B. Terent'ev, N. S. Ikonnikov, V. I. Dostovalova, and R. Kh. Freidlina, *Dokl. Akad. Nauk SSSR*, **213**, 1345 (1973).

(41) A. B. Terent'ev, M. A. Churilova, N. S. Ikonnikov, and R. Kh. Freidlina, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 439 (1975).

(42) N. S. Ikonnikov and A. B. Terent'ev, *Izv. Akad. Nauk SSSR, Ser. Khim.* 371 (1975).

(43) F. R. Mayo, *J. Am. Chem. Soc.*, **70**, 3689 (1948).

Table I

Chain-Transfer Coefficients and Isomerization Constants for Telomerizations of Ethylene Involving Radical Rearrangements

			Number of monomer units in radical					
No.	Telogen	$C \times 10^2$	1	2	3	4	C_i, M	Ref
1	CH_3COOCH_3	C_n	2.1	2.4	4.7	4.1	1.5	9
		C'_m			4.5	5.5		
		C_n^{sum}	2.1	1.4	4.6	3.3		
						(C_5^{sum} 4.5)		
2	CH_3CN	C_n	1.2	2.5	3.3	4.1	0.9	12
		C_n^{sum}	1.2	1.5	3.4	3.2		
3	$ClCH_2COOCH_3$	C_n	6.3	11.6	18.8	19.6	3.6	15
		C'_m			9.1	16.3		
		C_n^{sum}	6.3	4.8	12.6	17.3		
4	$BrCH_2COOCH_3$	C_n	72	96	114	120	0	9
5	CH_3CH_2COOH	C_n	10.0	12.0	14.0	15.0	6.5	44
		C'_m			16.0	19.0		
		C_n^{sum}	10.0	2.3	18.0	17.0		
6	$CH_3CH_2COOCH_3$	C_n	7.8	10.1	11.2	11.8	5.2	44
		C'_m			10.0	12.4		
		C_n^{sum}	7.8	4.3	10.6	12.2		
7	CH_3CH_2CN	C_n	9.9	10.1	9.0	7.7	2.9	44
		C'_m			9.5	11.0		
		C_n^{sum}	9.9	4.0	9.3	9.2		
8	$C_4H_9CH_2COOCH_3$	C_n	13.5	12.5	13.9	14.0	2.0	44
		C'_m			16.2	12.0		
		C_n^{sum}	13.5	5.7	15.1	12.8		
9	CH_3CH_2OH	C_n	5.4	3.2	4.0	4.4	0.3	45
		C'_m			7.3	7.1		
		C_n^{sum}	5.4	3.3	4.9	5.4		
10	$HCOOCH_3$[b]	C_n	2	4	13	14	0.4	33
		C'_m				8		
						($C_5 = 9$)		
		C_n[e]	5	9	14	15[c]		
11	ClCOCOCl	C_n	22	11000	700			34
12	$CNCH_2COOCH_3$	C_n	9.5	42			43	10
13	c-C_6H_{12}	C_n	7.6	10.3		$C_{n>2} = 8.6$	2.4	5
14	CCl_4[d]	C_n	40	670			0.2	20

[a] Initiating agent *tert*-butyl peroxide, 120–150 °C. [b] 1,6-hydrogen shift. [c] For the $HCO_2CH_2(CH_2CH_2)_n\cdot$ series. [d] Data obtained in the gas phase.

hydrogen abstraction. Thus, C_n^{sum} values can be used in identification of isomerizing species. In the case of methyl acetate, C_n^{sum} vs. n dependence features two minima at n of 2 and 4 indicative of repeated rearrangement (Table I, no. 1).

The $n \geq 3$ radicals which occur in telomerizations of ethylene, $\cdot(CH_2CH_2)_nCHRX$ (R is H, Cl, CH_3, C_4H_9; X is COOH, $COOCH_3$, CN, OH), have similar growth rate constants. The differences in the $C_{n\geq3}$ values depend mainly on the differences in the nature of telogens. This fact makes it possible to order telogens according to their reactivities in chain transfer: $Br{-}CH_2COOCH_3 > H{-}CHClCOOCH_3 > H{-}CH(CH_3)COOH \simeq H{-}CH(C_4H_9)COOCH_3 \simeq H{-}CH(CH_3)COOCH_3 > H{-}CH(CH_3)CN > H{-}CH(CH_3)OH \simeq H{-}CH_2COOCH_3$.

The effect of telogen reactivity on C_i is most manifest in the case of $BrCH_2COOCH_3$ and CH_3COOCH_3, which give the same radicals $\cdot(CH_2CH_2)_nCH_2COOCH_3$. The former telogen has C_3 of 1.14 and C_i of 0, while the latter has C_3 of 0.04 and C_i of 1.5 mol/l. (Table I, no. 1 and 4). Of telogens $RCH_2CO_2CH_3$, where R stands for H, Cl, or CH_3, methyl acetate is the least reactive one. Nevertheless, this compound is characterized by the lowest value of C_i in this series. This observation is indicative of the fact that the tendency toward rearrangement depends not only on telogen reactivity. The difference in stabilities of first-formed and isomer radicals is, seemingly, the determining factor in the case we are discussing: isomer radicals N (Scheme IX, c) are much more stable in the case of R = Cl or CH_3 than in the case of R = H, while stabilities of first-formed radicals N′ are to be approximately the same in the series. Another important factor influencing rearrangement of radicals, polarity of substituents in the α position relative to the carboxyl function, appears to be less important, since both methyl propionate and methyl chloroacetate give higher C_i values than methyl acetate.

A decrease in C_i on going from methyl propionate to methyl caproate (Table I, no. 6 and 8) may be due to steric factors. Intramolecular hydrogen abstraction in the growing radical $\cdot CH_2CH_2CH_2CH_2CHRCO_2CH_3$ should be hindered to a greater extent the longer the radical R.

Values of relative telomerization constants C_i, which are directly related to ratio of T_n to T'_m telomers produced in the reaction, are very essential for application of telomerization to syntheses of carboxylic acids branched at the α-carbon atom.

Use of Telomerization in Syntheses of Branched Compounds

Telomerizations involving radical rearrangements provide novel and widely applicable synthetic routes to branched compounds of various classes. A simple one-step procedure for the direct synthesis of α,α-dialkylcarboxylic acids (VIK) from acids of normal structure has been worked out[46] using the results from

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(44) R. Kh. Freidlina, A. B. Terent'ev et al., *Dokl. Akad. Nauk SSSR*, **208**, 1366 (1973).

(45) A. B. Terent'ev and M. A. Churilova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2593 (1972).

telomerization investigations reviewed in this Account. VIK acids are of considerable commercial interest. Their industrial applications depend strongly on structure of initial acids, number and structure of substituents present, and length of main chains. Three types of acids are obtained on an industrial scale: C_{5-9}, C_{11-19}, and $C_{>19}$. VIK are used in the production of oil-free coatings—lacquers and enamels for cars and household machinery—having good decorative and protective properties.[47] VIK have also found applications as extractants for isolation and separation of nonferrous and rare metals from aqueous solutions of their salts.[48]

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(46) R. Kh. Freidlina, A. B. Terent'ev, Yu. P. Chizhov, N. S. Ikonnikov, French Patent 1,537,490 (1967); *Chem. Abstr.*, **71**, 101319g (1969).

(47) R. Kh. Freidlina, A. B. Terent'ev, P. M. Bogatyrev et al., French Patent 2,091,907 (1974); *Chem. Abstr.*, **83**, 81407b (1975).

(48) A. V. Nikolaev, A. I. Khol'kin, R. Kh. Freidlina, A. B. Terent'ev et al., *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, 52 (1972).

Catalysis by Alloys and Bimetallic Clusters

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Bimetallic catalysts have been of interest for investigating the so-called "electronic factor" in catalysis by metals.[1-6] Transition metals, especially the metals of group 8, are the active catalysts for many reactions.[7] In terms of the electron-band theory, a group 8 metal such as nickel is characterized as having an incompletely filled d band, whereas a group 1B metal such as copper has a filled d band. According to the original view of Mott and Jones,[8] an alloy of a group 8 metal with a group 1B metal is characterized by a d band which is filled to a greater extent than that of the pure group 8 metal. In the case of a nickel–copper alloy, the substitution of copper atoms for nickel atoms in the metal lattice adds extra electrons to the lattice. The extra electrons introduced with the copper enter the d band until it is filled. By varying the composition of the alloy, one can alter the degree of filling of the d band with electrons and observe the effect on catalytic activity.

In the model of electronic structure just described for the alloys, which is known as the "rigid band" model, there is a single d band for the alloy as a whole, with no differentiation between the different types of atoms in the alloy with regard to their chemical bonding properties. This model of the electronic structure of group 8–group 1B metal alloys has been challenged in recent years.[9-12] According to the more recent view, there are separate d bands characteristic of each component of the alloy. In any case, the experimental data on chemisorption and catalysis indicate that the different types of atoms in the surface of the alloy, e.g., nickel and copper, retain their chemical differences, although bonding properties of the atoms are probably altered to some degree.[13] Present efforts to elucidate the electronic factor in catalysis by alloys are proceeding from this point of view, which resembles the idea of "ligand" effects in the chemistry of organometallic complexes.[14]

Although progress in the use of alloys to elucidate the electronic factor in metal catalysis has been slow, interest in bimetallic systems has not declined. In fact, there has been a great revival of interest in the field in recent years, for reasons other than a renewed probing into the electronic factor alone. These include (a) the realization that bimetallic systems may exhibit major selectivity effects in catalysis, i.e., markedly different behavior toward different types of reactions,[15-20] and (b) the development of the idea of highly dispersed bimetallic systems, i.e., "bimetallic cluster" catalysts.[17,21]

The selectivity features of bimetallic catalysts have only recently received any attention. Early studies of the electronic factor emphasized the relation between alloy composition and catalytic activity for hydrogenation reactions in which selectivity was not a consideration. Typical reactions investigated were the hydrogenation of benzene to cyclohexane[4] and ethylene to ethane.[5,6] It has now been shown that the addition of a group 1B metal to a group 8 metal decreases

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(1) G. M. Schwab, *Discuss. Faraday Soc.*, **8**, 166 (1950).

(2) D. A. Dowden, *J. Chem. Soc.*, 242 (1950).

(3) D. A. Dowden and P. Reynolds, *Discuss. Faraday Soc.*, **8**, 184 (1950).

(4) W. K. Hall and P. H. Emmett, *J. Phys. Chem.*, **62**, 816 (1958).

(5) W. K. Hall and P. H. Emmett, *J. Phys. Chem.*, **63**, 1102 (1959).

(6) R. J. Best and W. W. Russell, *J. Am. Chem. Soc.*, **76**, 838 (1954).

(7) J. H. Sinfelt, *Progr. Solid-State Chem.*, **10** (2), 55 (1975).

(8) N. F. Mott and H. Jones, "Theories of the Properties of Metals and Alloys", Oxford University Press, London, 1936.

(9) D. H. Seib and W. E. Spicer, *Phys. Rev. Lett.*, **20**, 1441 (1968).

(10) C. D. Gelatt and H. Ehrenreich, *Phys. Rev. B*, **10**, 398 (1974).

(11) P. Soven, *Phys. Rev.*, **156**, 809 (1967).

(12) B. Velicky, S. Kirkpatrick, and H. Ehrenreich, *Phys. Rev.*, **175**, 747 (1968).

(13) W. M. H. Sachtler and P. van der Plank, *Surf. Sci.*, **18**, 62 (1969).

(14) W. M. Sachtler, *LeVide*, **164**, 67 (1973).

(15) J. H. Sinfelt, J. L. Carter, and D. J. C. Yates, *J. Catal.*, **24**, 283 (1972).

(16) J. H. Sinfelt, A. E. Barnett, and J. L. Carter, U.S. Patent 3,617,518 (1971).

(17) J. H. Sinfelt, *J. Catal.*, **29**, 308 (1973).

(18) J. H. Sinfelt, Y. L. Lam, J. A. Cusumano, and A. E. Barnett, *J. Catal.*, **42**, 227 (1976).

(19) V. Ponec and W. M. H. Sachtler, *J. Catal.*, **24**, 250 (1972).

(20) J. M. Beelen, V. Ponec, and W. M. H. Sachtler, *J. Catal.*, **28**, 376 (1973).

(21) J. H. Sinfelt, *Chem. Eng. News*, **50**, 18 (July 3, 1972).