

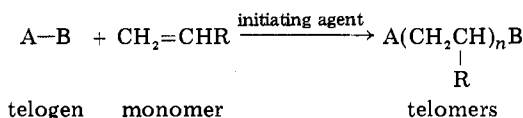
Free-Radical Rearrangements in Telomerization

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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



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 monograph¹ 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.

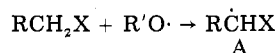
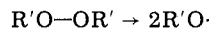
It was first discovered in 1964, in studies of telomerization of ethylene with acetic acid⁴ and cyclohexane,⁵

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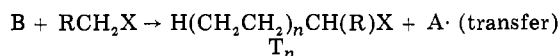
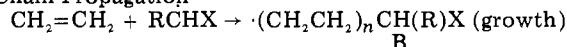
Professor Aleksandr Borisovich Terent'ev was born in Moscow in 1932 and graduated from the School of Chemistry, Moscow University. He received his Candidate of Chemical Sciences degree in 1963 and Doctor of Chemical Sciences in 1973, and is now with the Institute of Organo-Element Compounds. His studies are devoted to telomerization and radical rearrangements.

Scheme I Telomerization Mechanism^a

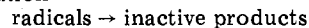
Initiation



Chain Propagation

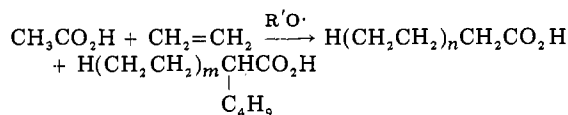


Chain Termination



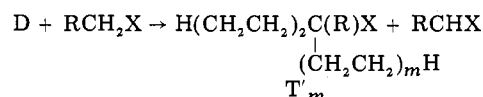
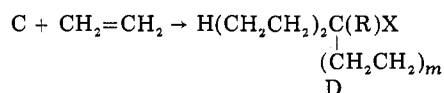
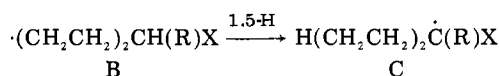
^a X is OH, COOR'', CN, etc. R is any substituent, n is 1, 2, 3, . . . T_n are telomers containing n monomer units in the chain.

Scheme II Telomerization of Ethylene with Acetic Acid



Scheme III^a

1,5 Hydrogen Shift in Growing Radicals



^a For notation, see Scheme I.

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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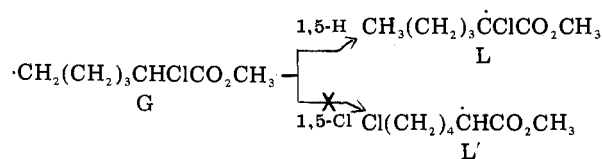
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Scheme VI

Radical Rearrangements in Telomerization of Ethylene with Methyl Chloroacetate



(C₄H₉)(CH₂CH₂)_nH (n = 1–3). The latter products originate from 1,5-hydrogen shifts in CH₃COOC-H₂(CH₂CH₂)₂· radicals. One of the earliest patents for telomerization of ethylene with acetic acid¹¹ also stresses the very complicated nature of the process. Telomerizations of ethylene^{7,12} and tetrafluoroethylene¹³ 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(CH₂CH₂)_nCH₂COOCH₃ (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-(CH₂CH₂)_nCHClCOOCH₃ (T_n, n = 1–5) along with rearrangement telomers H(CH₂CH₂)_m-C(C₄H₉)-ClCOOCH₃ (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 RCH₂X (where R stands for CH₃, C₂H₅, C₄H₉, and X is CO₂H, CO₂CH₃, 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 adipate.¹⁹ The first three compounds differ from those discussed above by the presence of reactive methylene groups CH₂XY (X and Y stand for COOCH₃, COOC₂H₅, CN, CH₃CO-) which enhance chain-transfer rates and lead to predominant formation of lower telomers.

Diethyl malonate reacts with ethylene to give H-(CH₂CH₂)_nCH(COOC₂H₅)₂ (n = 1–3) and R₁R₂C-(COOC₂H₅)₂ (where R₁ and R₂ stand for ethyl or butyl). Mechanistic interpretation of these results is not unambiguous because high reactivity of the C–H bonds in products H(CH₂CH₂)_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-CH₂CH₂CHXY. The Japanese authors¹⁰ 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 Cyclohexane⁵ 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.

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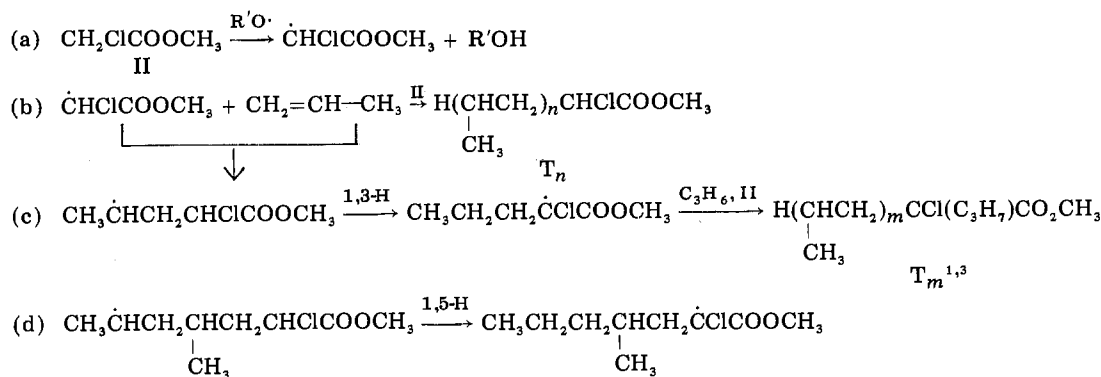
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Scheme VIII
Telomerization of Propylene with Methyl Chloroacetate



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 chloroacetate⁴⁰ 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 ¹³C 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 occur⁴² (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 (CH₃) 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 $\text{CH}_3\dot{\text{C}}\text{HCH}_2\text{CHClCO}_2\text{CH}_3$ radical which favor intramolecular chain transfer by the attack of the radical center nucleophile $\text{CH}_3\dot{\text{C}}\text{H}-$ on the $-\text{CHClCO}_2\text{CH}_3$ 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.

Kinetics of telomerization are usually described in terms of partial chain-transfer coefficients, $C_n =$

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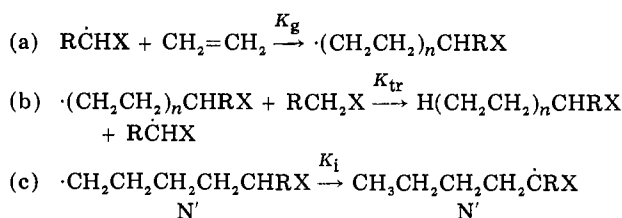
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(42) N. S. Ikonnikov and A. B. Terent'ev, *Izv. Akad. Nauk SSSR, Ser. Khim.* 371 (1975).

Scheme IX

Chain Propagation in Telomerization^a



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

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

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

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^{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^{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^{sum} with variation of n depends on the reaction pattern. With reactions involving 1,5-hydrogen shifts, the minimum value of C_n^{sum} corresponds to the $n = 2$ radical, the radical which undergoes intramolecular

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

No.	Telogen	$C \times 10^2$	Number of monomer units in radical				C_i, M	Ref
			1	2	3	4		
1	$\text{CH}_3\text{COOCH}_3$	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		
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	$\text{ClCH}_2\text{COOCH}_3$	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	$\text{BrCH}_2\text{COOCH}_3$	C_n	7.2	9.6	11.4	12.0	0	9
		C'_m			16.0	19.0		
5	$\text{CH}_3\text{CH}_2\text{COOH}$	C_n	10.0	12.0	14.0	15.0	6.5	44
		C'_m			18.0	17.0		
		C_n^{sum}	10.0	2.3	18.0	17.0		
6	$\text{CH}_3\text{CH}_2\text{COOCH}_3$	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	$\text{CH}_3\text{CH}_2\text{CN}$	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	$\text{C}_4\text{H}_9\text{CH}_2\text{COOCH}_3$	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	$\text{CH}_3\text{CH}_2\text{OH}$	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_n^e	5	9	14	15 ^c		
11	ClCOCOCI	C_n	22	11000	700			34
12	$\text{CNCH}_2\text{COOCH}_3$	C_n	9.5	42			43	10
13	$\text{c-C}_6\text{H}_{12}$	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 $\text{HCO}_2\text{CH}_2(\text{CH}_2\text{CH}_2)_n$ 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, $\cdot(\text{CH}_2\text{CH}_2)_n\text{CHRX}$ (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 $C_{n \geq 3}$ 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: $\text{Br-CH}_2\text{COOCH}_3 > \text{H-CHClCOOCH}_3 > \text{H-CH}(\text{CH}_3)\text{COOH} \approx \text{H-C-H}(\text{C}_4\text{H}_9)\text{COOCH}_3 \approx \text{H-CH}(\text{CH}_3)\text{COOCH}_3 > \text{H-C-H}(\text{CH}_3)\text{CN} > \text{H-CH}(\text{CH}_3)\text{OH} \approx \text{H-CH}_2\text{COOCH}_3$.

The effect of telogen reactivity on C_i is most manifest in the case of $\text{BrCH}_2\text{COOCH}_3$ and $\text{CH}_3\text{COOCH}_3$, which give the same radicals $\cdot(\text{CH}_2\text{CH}_2)_n\text{CH}_2\text{COOCH}_3$. 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 $\text{RCH}_2\text{CO}_2\text{CH}_3$, 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 $\cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CHRCO}_2\text{CH}_3$ 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 -di-alkylcarboxylic acids (VIK) from acids of normal structure has been worked out⁴⁶ using the results from

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(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

(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).

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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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 cyclohexane⁴ 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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