Nucleophilic Character of Alkyl Radicals. Part 17.[1] Absolute Rate Constants and the Alternating Effect in the Addition of Alkyl Radicals to Styrene and Acrylic Monomers

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The absolute rate constants for the addition of alkyl radicals to styrene and acrylic monomers are determined by two kinetic models. The first evaluates the ratio of electron-transfer oxidation by copper(II) acetate and addition to the double bonds, and the second determines the relative rates of alternating addition to acrylic monomers. The results are compared with the values in gas-phase reactions and are discussed in terms of polar effects and frontier orbital theory. The synthetic interest of the reactions involved is emphasized.

THE literature on addition rates of alkyl radicals to olefins is voluminous.[2] It is however mainly concerned with two fields: (i) reactions in the gas-phase, (ii) free-radical polymerization.[3] The two topics have interacted in the area of kinetics. On the other hand, very few data on the rates of alkyl radical addition to olefins, which do not involve free-radical polymerization, are known. Information on these last rates is of great importance from the mechanistic point of view because it provides a means of understanding the reactivity, selectivity, stability of the free-radicals involved, and the possible differences in gas-phase and solution reactions; moreover it allows new syntheses starting from cheap materials, such as vinyl monomers. In this paper we report the results obtained for the addition of primary alkyl radicals to styrene and in alternating addition to acrylic monomers and styrene.

RESULTS AND DISCUSSION

The possibility of using free-radical reactions involving reactive vinyl monomers without polymerization, copolymerization, and telomerization depends on the subsequent ability of the adduct radical to engage in a radical transfer competitive reaction faster than in propagation. Thus we [4] have previously determined the absolute rate constants for the addition of alkyl radicals to acrylonitrile and acrylate by product analysis [(0) and (I) (Scheme 1)]. The possibility of obtaining compounds

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[1] Part 16, A. Citterio, F. Minisci, O. Porta, and G. Sesana, *J. Amer. Chem. Soc.*, 1977, **99**, 7960.

[2] P. I. Abell, ' Comprehensive Chemical Kinetics ' eds. C. H. Bamford and C. F. H. Tipper, Elsevier, Amsterdam, 1976, vol. 18, p. 147.

[3] T. Alfrey, jun. and L. J. Young, ' Copolymerization 'in ' High Polymers,' ed. G. E. Ham, Wiley, New York 1964, vol. XVIII, ch. 2; A. D. Jenkins, *Adv. Free Radical Chem.*, 1967, 2, 139; J. M. Tedder, ' Reactivity and Mechanism in Polymer Chemistry,' eds. A. D. Jenkins and A. Ledwith, Wiley, London 1974, ch. 2.

[4] T. Caronna, A. Citterio, M. Ghirardini, and F. Minisci, *Tetrahedron*, 1977, **33**, 793.

like (I) is related to the fact that k_{ox}' [equation (5)] is considerably greater than k_p [the rate of addition of the radical adduct (A) to a further molecule of olefin forming a telomer radical (B)]. This kinetic model has however a severe limitation in the fact that the values of k_{ox} [equation (2)] are very high, close to the diffusion-controlled limit (1.1×10^9 and 3.6×10^8 mol l^{-1} s^{-1} at 25 °C, respectively, for X = Cl and SCN).[5]

TABLE 1

Absolute rate constants at 25 °C of n-heptyl radical addition to some vinyl derivatives [data for $CH_3COOH-CH_3CN$ (3 : 2) solutions]

Monomer	$k_{abs.}$/ mol l^{-1} s^{-1}
Styrene	9.3×10^4
Methyl acrylate	2.2×10^5
Acrylonitrile	5.9×10^5
Acrylic acid	6.8×10^5
Methacrylic acid	7.3×10^5

TABLE 2

Relative rates of n-heptyl and polystyryl radicals toward some vinyl derivatives and copolymerization data [2]

Monomer	r_1	r_2	Polystyryl radical [2] at 60 °C	n-Heptyl radical at 25 °C
Styrene			1	1
Methyl acrylate	0.70	0.18	1.4	2.4
Acrylonitrile	0.40	0.03	2.5	6.3
Acrylic acid	0.15	0.35	6.3	7.3
Methacrylic acid	0.15	0.7	6.3	7.8

$$RCOO{-}OCOR + Cu^+ \longrightarrow R^{\bullet} + CO_2 + RCOO^- + Cu^{2+} \qquad (1)$$

$$R^{\bullet} + CuX^+ \xrightarrow{k_{ox}} \underset{(0)}{RX} + Cu^+ \qquad (2)$$

$$R^{\bullet} + CH_2{=}CH{-}CN \xrightarrow{k_{an}} RCH_2{-}\dot{C}H{-}CN\ (A) \qquad (3)$$

$$(A) + CH_2{=}CH{-}CN \xrightarrow{k_p} RCH_2{-}CH(CN){-}CH_2{-}\dot{C}H{-}CN\ (B) \qquad (4)$$

$$(A) + CuX^+ \xrightarrow{k_{ox}'} \underset{(I)}{RCH_2{-}CHX{-}CN} + Cu^+ \qquad (5)$$

$$X = Cl \text{ or } SCN$$

SCHEME 1

Thus with styrene, which is less reactive than acrylonitrile towards alkyl radicals, the model is not suitable because, even with very low concentration of copper(II) halide, the amount of addition product is too small for rigorous kinetic treatment.

We have therefore chosen a similar kinetic model based on the chain reactions of Scheme 2. In this case the possibility of obtaining compounds (III) and (IV) is related to the fact that the electron-transfer oxidation [k_{ox} of equation (6) is 1.6×10^5 mol l^{-1} s^{-1} at 25 °C] is slower [6] than the ligand-transfer oxidation [equation (2)] and the oxidation of the benzylic radical [equation (8)] is much faster than propagation of styrene polymerization. The reactions based on Scheme 2 are very clean, and only compounds (II)—(IV) and n-octanoic acid are formed for an appropriate concentration range of styrene and copper(II) salt.

At room temperature both steps (6) and (7) are irreversible and thus, steady-state treatment leads to the simple equation (a) for small conversions of styrene (f = final, i = initial).

$$(C_7H_{15}COO)_2 + Cu^+ \longrightarrow C_7H_{15}^{\bullet} + CO_2 + C_7H_{15}COO^- + Cu^{2+} \qquad (1)$$

$$C_7H_{15}^{\bullet} + Cu^{2+} \xrightarrow{k_{ox}} \underset{(II)}{C_5H_{11}CH{=}CH_2} + H^+ + Cu^+ \qquad (6)$$

$$C_7H_{15}^{\bullet} + CH_2{=}CHC_6H_5 \xrightarrow{k_{as}} C_7H_{15}CH_2{-}\dot{C}HC_6H_5 \qquad (7)$$

$$C_7H_{15}CH_2{-}\dot{C}HC_6H_5 + Cu^{2+} \xrightarrow{k_{ox}''} C_7H_{15}CH_2\overset{+}{C}HC_6H_5 + Cu^+ \qquad (8)$$

$$C_7H_{15}CH_2{-}\overset{+}{C}HC_6H_5 \longrightarrow \underset{(III)}{C_7H_{15}CH{=}CHC_6H_5} + H^+ \qquad (9)$$

$$C_7H_{15}CH_2{-}\overset{+}{C}HC_6H_5 + CH_3COOH \longrightarrow \underset{(IV)}{C_7H_{15}CH_2{-}CHC(OCOCH_3)_6H_5} + H^+ \qquad (10)$$

SCHEME 2

$$([(III)]_f + [(IV)]_f)/[(II)]_f = k_{as}[\text{styrene}]_i/k_{ox}[Cu^{2+}] \qquad (a)$$

Plots of the ratio $([(III)]_f + [(IV)]_f)/[(II)]_f$, from Tables 3 and 4, against styrene and copper(II) initial concentrations afford linear graphs, which enable us to evaluate k_{as}/k_{ox}. After correction, due to the monomer–dimer equilibrium of the copper(II) acetate,[6] a value of 9.3 10^4 mol l^{-1} s^{-1} was obtained for k_{as} at 25 °C.

TABLE 3

Alkylation rates of styrene by di-n-octanoyl peroxide (6×10^{-3}M) catalysed by CuOAc (3×10^{-3}M) in the presence of $Cu(OAc)_2$ (0.024M) [$CH_3COOH-CH_3CN$ (3 : 2), 25 °C]

[Styrene]/M	Product (mole %) (I)	(II)	(III)	(IV)	$\frac{(III) + (IV)}{(II)}$	k_{as}/k_{ox} [a]
0.60	0.6	11.8	83.0	5.0	7.5	0.0990
0.51	0.7	13.9	78.0	4.0	5.9	0.0924
0.40	0.8	16.3	76.5	4.2	4.9	0.0970
0.25	0.8	22.7	70.5	4.1	3.3	0.1043
0.25	0.9	21.2	61.5	3.8	3.1	0.0980
0.20	0.8	30.3	62.5	3.6	2.2	0.0975

[a] Standard deviations, for individual kinetic runs were in the range 3—5% with good agreement between duplicate runs.

TABLE 4

Alkylation rates of styrene (0.25M) by di-n-octanoyl peroxide (6 10^{-3}M) catalysed by CuOAc (3×10^{-3}M) in the presence of $Cu(OAc)_2$ [$CH_3COOH-CH_3CN$ (3 : 2), 25 °C]

$[Cu(OAc)_2]$/M	Product (mole %) (I)	(II)	(III)	(IV)	$\frac{(III) + (IV)}{(II)}$	k_{as}/k_{ox}
0.012	0.6	13.5	71.5	5.0	5.6	0.0884
0.024	0.8	22.7	70.5	4.1	3.3	0.1034
0.024	0.9	21.2	61.5	3.8	3.1	0.0980
0.032	a	23.6	64.0	4.0	2.8	0.1181
0.052	a	35.4	53.5	3.1	1.6	0.1089
0.096	a	54.0	42.3	2.7	0.9	0.1139

[a] <0.5%.

A different kinetic study to determine k_{as} was carried

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[5] J. K. Kochi and R. V. Subramamian, *J. Amer. Chem. Soc.*, 1965, **87**, 1508, 4805.

[6] C. L. Jenkins and J. K. Kochi, *J. Amer. Chem. Soc.*, 1972, **94**, 843.

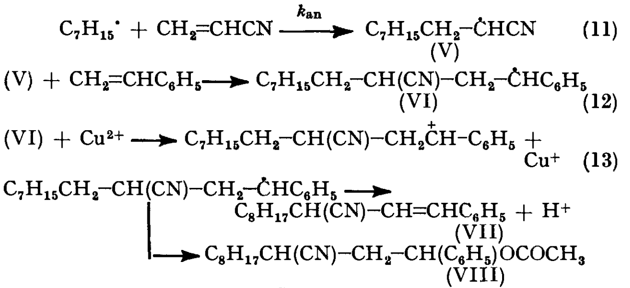
TABLE 5

Free radical alkylation of acrylonitrile and styrene by di-n-octanoyl peroxide (0.012M) catalysed by copper(I) acetate (0.008M) [$CH_3COOH–CH_3CN$ (3 : 2), 25 °C]

		Product (mole %)								
[Acrylonitrile]/M	[Styrene]/M	(III)	(IV)	(VII)	(VIII)	(II)	$\frac{(VII) + (VIII)}{(III) + (IV)}$	k_{an}/k_{as}	k_{as}/k_{ox} *	k_{an}/k_{ox} *
0.051	0.25	3.0	28	2.0	37	19	1.24	6.2	0.5 + 0.1	2.7 + 0.5
0.102	0.25	2.0	20	3.0	55	14	2.64	6.7		
0.150	0.25	1.5	16.5	3.0	65	11	4.00	6.8		
0.210	0.25	1.0	14	4.0	72	9	5.06	6.0		
0.070	0.25	3.0	26	3.0	47	17	1.70	6.1		
0.120	0.25	2.0	18	3.0	59	12	3.10	6.5		

* By least squares analysis from equation (b).

out by direct competition of the n-heptyl radical in the addition to styrene and acrylonitrile. In this case equations (11)—(13) of Scheme 3 must be included in



$$C_7H_{15}^{\cdot} + CH_2{=}CHCN \xrightarrow{k_{an}} \underset{(V)}{C_7H_{15}CH_2{-}\dot{C}HCN} \quad (11)$$

$$(V) + CH_2{=}CHC_6H_5 \longrightarrow \underset{(VI)}{C_7H_{15}CH_2{-}CH(CN){-}CH_2{-}\dot{C}HC_6H_5} \quad (12)$$

$$(VI) + Cu^{2+} \longrightarrow C_7H_{15}CH_2{-}CH(CN){-}CH_2\overset{+}{C}H{-}C_6H_5 + Cu^{+} \quad (13)$$

$$C_7H_{15}CH_2{-}CH(CN){-}CH_2{-}\dot{C}HC_6H_5 \longrightarrow \underset{(VII)}{C_8H_{17}CH(CN){-}CH{=}CHC_6H_5} + H^{+}$$

$$\longrightarrow \underset{(VIII)}{C_8H_{17}CH(CN){-}CH_2{-}CH(C_6H_5)OCOCH_3}$$

SCHEME 3

Scheme 2. The quantitative determination of heptene and the alkylation products (III), (IV), (VII), and (VIII) enable the absolute rate constants k_{as} and k_{an} to be obtained.

The validity of the kinetic model in this case is based on the fact that radical (V) has electrophilic character, due to the proximity of the cyano-group to the radical centre, and reaction (12) takes place much faster than both the oxidation of radical (V) by copper(II) salt and the propagation reaction.[7] This is an aspect of the alternating effect in free-radical copolymerization. Moreover the electron-transfer oxidation (13) is the only reaction of the benzylic radical (VI) because it is much faster than addition of the same radical to both styrene and acrylonitrile, preventing in this way polymerization, copolymerization, and telomerization. Assuming that both steps (7) are irreversible, equation (b) is derived

$$R = \frac{[(III)] + [(IV)] + [(VII)] + [(VIII)]}{[\text{heptene}]} = \frac{k_{as}[\text{styrene}]}{k_{ox}[Cu(OAc)_2]} + \frac{k_{an}[\text{acrylonitrile}]}{k_{ox}[Cu(OAc)_2]} \quad \text{(b)}$$

from steady-state treatment for low conversions of the olefins. By least square analysis of the data in Table 5, $k_{an}/k_{ox} = 3.7 \pm 0.5$ and $k_{as}/k_{ox} = 0.5 \pm 0.1$ can be evaluated from the slope and intercept of equation (b). From the value of k_{ox}[5] we obtained k_{an} 6.8 × 10^5 and k_{as} 0.8 × 10^5 mol l^{-1} s^{-1}.

Relative rates are more easily derived, imposing the steady state condition for radical adducts, from equation (c). A mean value of 6.3 was obtained for relative rate

$$\frac{[(VII)]_f + [(VIII)]_f}{[(III)]_f + [(IV)]_f} = \frac{k_{an}[\text{acrylonitrile}]_i}{k_{as}[\text{styrene}]_i} \quad \text{(c)}$$

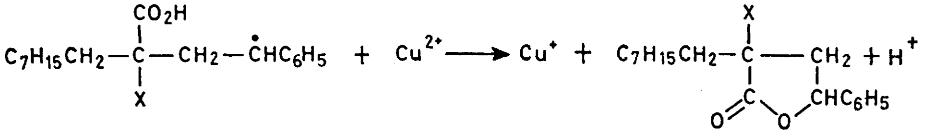
of addition of n-heptyl radical to acrylonitrile *versus* addition to styrene.

We[4] have previously determined k_{an} for two different kinetic models; the values obtained (5.2 and 5.9 × 10^5 mol l^{-1} s^{-1} at 0 °C) are in good agreement with that derived from this treatment.

Similar kinetic models were used with methyl acrylate and acrylic and methacrylic acid. The reaction is particularly interesting with last two monomers because only the lactones (IX) and (X) are formed in the alternating addition [equation (14)]. With methyl acrylate, in addition to the ester (XI), a high yield of lactone (IX) is formed from benzylic cation intramolecular attack. Plots of the ratios $\{[(III)]_f + [(IV)]_f\}/[(IX)]_f$, $([III)]_f +$

$$\underset{(XI)}{C_7H_{15}CH_2{-}CH(CO_2Me){-}CH_2{-}CH(C_6H_5){-}OCOCH_3}$$

$[(IV)]_f)/[(X)]$, and $([(III)]_f + [(IV)]_f)/([(IX)]_f + [(XI)_f]\}$, given in Tables 6—8, against the ratio of styrene/acrylic acid, styrene/methacrylic acid, and styrene/methyl acrylate concentrations afford linear graphs. These plots enable the rate constants of the addition of n-heptyl radical to acrylic acid (k_{aa}), methacrylic acid (k_{am}), and methyl acrylate (k_{ac}) to be evaluated.



(14)

(IX) X = H

(X) X = CH_3

Table 1 gives the absolute rate constants at 25 °C for the monomers investigated. The value for the rate of

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[7] F. Minisci, *Accounts Chem. Res.*, 1975, **8**, 165.

TABLE 6

Free radical alkylation of acrylic acid and styrene by di-n-octanoyl peroxide (0.012M) catalysed by copper(I) acetate (0.008M) [CH_3COOH–CH_3CN (3 : 2), 25 °C]

[Acrylic acid]/M	[Styrene]/M	Product (mole %) (III)	(IV)	(IX)	(II)	$\frac{(IX)}{(III) + (IV)}$	k_{aa}/k_{as}	k_{as}/k_{ox} *	k_{aa}/k_{ox} *
0.050	0.25	3.0	32	47	18	1.35	6.75	0.56 ± 0.05	4.3 + 0.5
0.105	0.25	1.5	14	61	10	3.95	7.91		
0.151	0.25	2.0	14	68	8	4.46	7.36		
0.195	0.25	1.0	12	74	7	5.70	7.24		

* By least squares analysis from equation (b).

TABLE 7

Free radical alkylation of methacrylic acid and styrene by di-n-octanoyl peroxide (0.012M) catalysed by copper(I) acetate (0.008M) [CH_3COOH–CH_3CN (3 : 2), 25 °C]

[Mathacrylic acid]/M	[Styrene]/M	Product (mole %) (III)	(IV)	(X)	(II)	$\frac{(X)}{(III) + (IV)}$	k_{am}/k_{as}	k_{as}/k_{ox} *	k_{am}/k_{ox} *
0.051	0.25	2.0	25	44	17	1.63	8.01	0.45 + 0.05	4.5 + 0.5
0.102	0.25	2.0	19	70	13	3.32	8.32		
0.151	0.25	3.0	13	71	11	4.44	7.35		
0.071	0.25	2.5	22	53	14	2.16	7.75		

* By least squares analysis from equation (b).

TABLE 8

Free radical alkylation of methyl acrylate and styrene by di-n-octanoyl peroxide (0.012M) catalysed by copper(I) acetate (0.008M) [CH_3COOH–CH_3CN (3 : 2), 25 °C]

[Methyl acrylate]/ M	[Styrene]/M	Product (mole %) (III)	(IV)	(IX)	(XI)	(II)	$\frac{(IX) + (XI)}{(III) + (IV)}$	k_{ac}/k_{as}	k_{as}/k_{ox} *	k_{ac}/k_{ox} *
0.050	0.25	4.0	47	22	2	16	0.47	2.35	0.5 + 0.1	1.4 + 0.3
0.105	0.25	3.0	35	37	3	10	1.06	2.52		
0.150	0.25	3.0	33	53	4	9	1.60	2.40		
0.210	0.25	2.4	22	49	4	6	2.08	2.43		

* By least squares analysis from equation (b).

addition to methyl acrylate is in agreement with that previously obtained.[4] In Table 2 the relative rates, calculated from Table 1, of n-heptyl and polystyryl radical towards the same olefins together with copolymerization data [2] are reported. We attempted to determine the temperature dependence of the rate constants, but unfortunately the kinetic model was not suitable, due to the particular effect upon the oxidation constants of the alkyl radicals by Cu^{2+}, which prevents a study over a significant range of temperature.

The results obtained clearly indicate that all the acrylic monomers are more reactive than styrene towards alkyl radicals. The values (extrapolated to 25 °C) reported for gas-phase addition of ethyl radical to acrylonitrile [8] and styrene [8] follow the same sequence but the rate constants are slightly lower than those found by us in solution.

The high rates and the sequence obtained can be explained in terms of intermediate radical stability and polar effects. Alkyl radicals react with these monomers faster than with unconjugated [3] olefins (no significant addition product was in fact obtained under similar conditions) because both benzylic and α-cyano- or α-carboxy-alkyl radicals are resonance stabilized. The higher reactivity of acrylic monomers must be ascribed to polar effects due to the nucleophilic character of the alkyl radicals. The polar forms (XII) and (XIII) contribute to the transition state decreasing in significant way the addition activation energy. On the other hand,

$$[R^{1\bullet}\ CH_2{=}CH{-}COOR^2] \longleftrightarrow \underset{(XII)}{[R^{1+}\ (CH_2\overset{\cdots}{-}CH\overset{\cdots}{-}COOR^2)^{\bullet -}]}$$

$$[R^{\bullet}CH_2{=}CH{-}CN] \longleftrightarrow \underset{(XIII)}{[R^{+}(CH_2\overset{\cdots}{-}CH\overset{\cdots}{-}CH)^{\bullet -}]}$$

the α-cyano- and α-carboxy-alkyl radicals have electrophilic character and attack styrene exclusively, which is the electron richer olefin, because of the contribution of the polar form (XIV).

$$[-\dot{C}H(CN)^{\bullet}\ CH_2{=}CH{-}C_6H\ ] \longleftrightarrow \underset{(XIV)}{[-\bar{C}H(CN)CH_2\overset{\cdots}{-}CH\overset{\cdots}{-}C_6H^{\bullet +}]}$$

In terms of frontier orbital theory, the electrophilic α-cyano alkyl radical has a lower energy SOMO than that of nucleophilic alkyl radical (these energies are in fact given roughly by ionization potentials of the corresponding radicals: 8.04 for primary alkyl radicals [9] and 9.15 eV for α-cyano alkyl radicals [10]). Acrylic monomers have HOMO and LUMO energies lower than those of ethylene and styrene, so that we can expect stronger interaction between the SOMO of the alkyl radical and the LUMO of acrylic monomers compared with styrene.

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[8] D. G. L. James and D. McCallum, *Canad. J. Chem.*, 1965, **43**, 640.

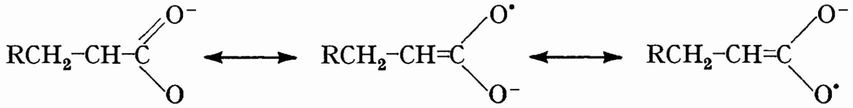
[9] P. F. Lossing, P. Kerarle, and J. B. DeSouse, ' Ionization Potentials of Alkyl and Halogenated Alkyl Free Radicals,' *Adv. Mass Spectrometry*, 1959, **1**, 431.

[10] R. F. Petric and F. P. Lossing, *J. Amer. Chem. Soc.* 1961, **83**, 4737.

For analogous reasons the interaction between the SOMO of α-cyanoalkyl radicals and the HOMO of styrene is reinforced with acrylic monomers; this contributes to the selectivity of reaction (12) in agreement with the alternating effect of free-radical copolymerization.

In the series of acrylic monomers, however, the polar order does not hold. Acrylonitrile, the most electron-deficient among the investigated monomers, is more reactive than methyl acrylate, but less reactive than acrylic and methacrylic acid. In our opinion this higher reactivity can be explained by the fact that α-carboxyalkyl radical is a stronger acid than an aliphatic carboxylic acid owing to the sp^2 hybridization of the carbon atom near the carboxy-group: this gives higher resonance stabilization of the radical anion.

$$RCH_2\text{-}\dot{C}H\text{-}COOH \rightleftharpoons RCH_2\text{-}\dot{C}H\text{-}COO^- + H^+$$



The rate sequence obtained, summarized in Table 1, agrees with the results of styrene colopymerization with acrylic monomers based on the relative rate determination of the four propagation reactions (d)—(g). In

$$PM_1^{\bullet} + M_1 \xrightarrow{k_{11}} PM_1\text{-}M_1^{\bullet} \qquad (d)$$

$$PM_2 + M_2 \xrightarrow{k_{22}} PM_2\text{-}M_2^{\bullet} \qquad (e)$$

$$PM_1^{\bullet} + M_2 \xrightarrow{k_{12}} PM_1\text{-}M_2^{\bullet} \qquad (f)$$

$$PM_2^{\bullet} + M_1 \xrightarrow{k_{21}} PM_2\text{-}M_1^{\bullet} \qquad (g)$$

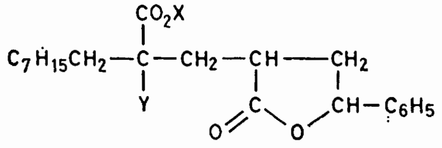
$$r_1 = k_{11}/k_{22}$$

$$r_2 = k_{12}/k_{21}$$

Table 2 the reactivity ratios (r_1 and r_2) and the relative rates of styrene (M_1) and acrylic monomers (M_2) are reported. The same sequence shows that both polystyryl radical, $PCH_2\dot{C}HC_6H_5$, and n-heptyl radical have nucleophilic character. However it is surprising that the selectivity of a primary alkyl radical is higher than that of a secondary benzyl radical because the latter is more nucleophilic and considerably less reactive (k_{11} for homopolymerization of styrene is about three orders of magnitude lower than k_{as} [11]). The comparison is not rigorous owing to the different conditions and the penultimate effect [12] on the styryl radical $PCH_2CHX\text{-}CH_2\text{-}\dot{C}HC_6H_5$, but we think the uncertainty in our kinetic model is lower than that for copolymerization kinetics.

The reactivity ratio r_2 is considerably lower for acrylonitrile than for the other acrylic monomers in agreement with the greater electrophilic character of the α-cyanoalkyl radical, due to the higher electron-withdrawing power of the cyano- compared with the carboxy-group. It follows that for acrylic and methacrylic acid, methyl acrylate, and to a lower extent acrylonitrile, an excess of acrylic monomer determines the formation of increasing amounts of the telomers (XV)—(XVIII). These products (isolated in preparative reactions to evaluate the extent of telomerization in kinetic experiments) become important (10—30% yield) at high conversion and with an excess (2—3 times) of the acrylic monomer.

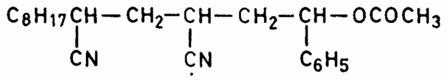
From the synthetic point of view, knowledge of the rate constants k_{ox}, k_{as}, k_{an}, k_{aa}, k_{ac}, and k_{am} allows a choice of the best experimental conditions and reagent ratios to prepare variable amounts of (III), (IV), and (VIII)—(X), minimizing the yield of (II) in the alternating addition to acrylic monomers and styrene. It is possible to obtain only (III) and (IV) in the absence of acrylic monomers and virtually only (VIII)—(X) with appropriate ratios of acrylic monomer/styrene. Moreover the alternating effect is not limited to addition to the investigated monomers only, but also other important industrial olefins, such as butadiene, methylbutadiene, α-methylstyrene, other acrylic monomers, maleic anhydride *etc.* Thus relatively complex compounds of structures such as (VIII)—(X) can be obtained simply starting from cheap materials, such as vinyl monomers.



(XV) X = Y = H

(XVI) X = CH3, Y = H

(XVII) X = H, Y = CH3



$$C_8H_{17}CH(CN)\text{-}CH_2\text{-}CH(CN)\text{-}CH_2\text{-}CH(C_6H_5)\text{-}OCOCH_3$$

(XVIII)

EXPERIMENTAL

General Method.—I.r. spectra were taken with a Perkin-Elmer 177 spectrophotometer, n.m.r. spectra with an A60 (or A100) Varian spectrometer in CCl_4 solution using tetramethylsilane as internal standard. Mass spectra were obtained on a Hitachi–Perkin-Elmer RMU-6D spectrometer at 70 eV with an all glass inlet system at 200 °C. Quantitative gas chromatograms were obtained with a Hewlett–Packard 5 850 instrument using 15 ft × $\frac{1}{8}$ in 10% UCC W on Chromosorb W AW-DMCS, 20 ft × $\frac{1}{8}$ in 2% XE60 on Chromosorb W AW-DMCS, and 15 ft × $\frac{1}{8}$ in 10% DEGS on Chromosorb DMCS, columns.

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[11] C. E. H. Bawn, 'Kinetics of Free Radical Polymerization' Pergamon, Oxford 1966, vol. 1.

[12] N. C. Billingham and A. D. Jenkins, 'Comprehensive Chemical Kinetics,' eds. C. H. Bamford and C. F. H. Tipper, Elsevier, Amsterdam, 1976, vol. 14, pp. 427—428.

Materials.—Acetic acid and acetonitrile were distilled twice over P_2O_5. Styrene, acrylonitrile, methyl acrylate, and acrylic and methacrylic acid were redistilled under nitrogen at 40 mmHg before use. Hept-1-ene and n-heptane were identified by comparison with authentic samples. No heptyl acetate was found in the reaction mixture ($<1\%$). Di-n-octanoyl peroxide, m.p. 23 °C, was prepared [13] by treatment of n-octanoyl chloride with H_2O_2–pyridine, and crystallized (ethanol–benzene) at 0 °C (purity 99% by iodometric analysis). Stock solutions of $Cu(OAc)_2$ (0.11M), styrene (1.0M), and n-octanoyl peroxide (0.012M) were made up in CH_3COOH–CH_3CN (3 : 2). Stock solution of copper(I) acetate (0.16M) was prepared by stirring copper (5 g) and $Cu(OAc)_2$ (14.00 g) in deoxygenated CH_3COOH–CH_3CN (3 : 2; 250 ml) under nitrogen; the colourless solution was standardized against 0.1N-$Ce(SO_4)_2$.

General Procedure for Preparative Alkylation of Vinyl Derivatives.—A solution of styrene (0.025 mol), acrylic monomer (0.02 mol), and copper(II) acetate (0.002 5 mol) was made up in CH_3COOH–CH_3CN (3 : 2) (70 ml), thermostatted at 25 °C, magnetically stirred, and flushed with nitrogen for 15 min. To this solution were added stock solution of copper(I) acetate (10 ml) and after 2 h a solution (20 ml) of peroxide (0.01 mol) in degassed CH_3COOH–CH_3CN. The reaction was continued until CO_2 was no longer evolved and the solution was evaporated to 20 ml at 60 °C under reduced pressure. The residue was dissolved in water (50 ml) and extracted twice with pentane–ether. The extracts were washed twice with 10% NaOH and with water, dried, and evaporated. The residue was analysed by g.l.c. and chromatographed on silica gel, eluting with hexane or hexane–ethyl acetate (9 : 1). The pure samples isolated (40—75%) were distilled and used to check the quantiative response to g.l.c.

1-*Phenylnonyl acetate*. This was prepared using styrene (yield 75%), b.p. 118 °C at 0.5 mmHg, $\nu_{max.}$ (film) 1 740, 1 240 (CH_3COO), $\delta(CCl_4)$ 7.3 (5 H, s, C_6H_5), 5.7 (1 H, t, CH), 1.9 (3 H, s, $COCH_3$), and 0.8—1.9 (17 H, m), *m/e* 262 ($M^{\cdot+}$), 220, 202, 149 (100%), 117, 91, 79, and 43, m^* 184.7 (262 ⟶ 220). The product was identical with a sample prepared by solvolysis in CH_3COOH of 1-bromo-1-phenylnonane, b.p. 122 °C at 0.1 mmHg, obtained by photochemical bromination [14] of 1-phenylnonane with CCl_3Br. The reaction gives as byproduct 1-phenylnon-1-ene (6%), b.p. 123—126 °C at 1 mmHg, a pure sample of which was prepared from 1-bromo-1-phenylnonane by elimination of HBr with alcoholic KOH.

1-*Phenyl*-3-*cyanoundecyl acetate*. This was prepared (65%) in the reaction with styrene and acrylonitrile, b.p. 181 °C at 1 mmHg, $\nu_{max.}$ (film) 2 250 (CN), 1 740, and 1 240 (CH_3COO) cm^{-1}, δ (CCl_4) 7.3 (5 H, m, C_6H_5), 5.90 (1 H, t, *J* 6.5 Hz, CHO), 205 (3 H, s, $COCH_3$), 2.17 (1 H, quintet, CHCN), and 0.8—1.6 (19 H, m), *m/e* 315 ($M^{\cdot+}$), 273, 256, 163, 149, 121, 107, and 43 (Found: C, 75.1; H, 9.8; N, 4.7. $C_{19}H_{29}O_2N$ requires C 75.2; H, 9.65; N, 4.6%). Preparative g.l.c. isolated 1-phenyl-3-cyanoundec-1-ene, *m/e* 255 ($M^{\cdot+}$). 1-Phenyl-3,5-dicyanotridecyl acetate (2%) was also isolated, $\nu_{max.}$ 2 250, 1 740, and 1 240 cm^{-1}; δ (CCl_4) 7.2 (5 H, s, C_6H_5), 5.8 (1 H, t, CH–O), 1.8 (3 H, s, $COCH_3$), 1.5—2.5 (4 H, m), and 0.8—1.5 (19 H, m), *m/e* 368($M^{\cdot+}$), 326, 325, 214, 162, 148, 121, 107, 91, and 43. Using twice the concentration of acrylonitrile this last product was isolated in 25% yield.

1-*Phenyl*-3-*n*-*octylbutyrolactone* (IX). This was isolated from the reaction of acrylic acid and styrene (60%), m.p. 67—68 °C (from light petroleum), $\nu_{max.}$ (KBr) 1 765 (CO lactone), δ ($CDCl_3$) 7.3 (5 H, s, C_6H_5), 5.36 (1 H, dd *J* 5.2, 10.5 Hz, CHO), 2.5—3.0 (2 H, m, C*H*$_2$CH), 2.2 (1 H, m, CHCO), and 0.8—1.6 (15 H, m), *m/e* 274 ($M^{\cdot+}$), 229, 170, 162 (100%), 152, 117, 104, 91, 77, 55, and 43 (Found: C, 79.8; H, 9.2. $C_{19}H_{26}O_2$ requires C, 79.7; H, 9.15%). After acidification of basic aqueous layer a small amount (3—4%) of 1-phenyl-3-(1-carboxy-n-nonyl)butyrolactone (XV) was isolated, $\nu_{max.}$ 3 100—2 700 and 1 765 cm^{-1}, *m/e* 346, 329, 302, 234, 202, 162, 117, 91, 77, and 55.

Compound (IX) was also the main product (55%) in the alkylation of methyl acrylate (0.04 mol). Byproducts of this reaction are methyl 2-(1-acetoxy-1-phenylethyl)-n-decanoate (5%), b.p. 165 °C at 0.1 mmHg, $\nu_{max.}$ 1 740, 1 240, and 1 165 cm^{-1}, *m/e* 348, 302, 288, 236, 162, 117, 91, and 77, and 1-phenyl-3-(2-carboxymethyl-n-decyl)butyrolactone (XVI) (15%), $\nu_{max.}$ 1 780, 1 740, and 1 165 cm^{-1} δ (CCl_4) 7.2 (5 H, m, C_6H_6), 5.3 (1 H, dd, C*HO*), 3.58 (3 H, s, OMe), 2.0—2.5 (4 H, m), and 0.8—1.8 (19 H, m), *m/e* 360 ($M^{\cdot+}$), 328, 310, 300, 216, 202, 160, 115, 101, 85, 73, 60, and 43. This product was present in less than 5% in all kinetic experiments.

1-*Phenyl*-3-*methyl*-3-*n*-*octylbutyrolactone*. This had m.p. 43—44 °C, $\nu_{max.}$ (film) 1 780 cm^{-1}, δ (CCl_4) 7.3 (5 H, m, C_6H_5), 5.32 (1 H, dd, *J* 6.5, 9.9 Hz), 2.0—2.4 (2 H, dd, ABX, C*H*$_2$CHO), and 0.8—1.6 (20 H, m), *m/e* 288 ($M^{\cdot+}$), 242, 202, 176, 131 (100%), 104, 91, 56, and 43. This reaction with methacrylic acid and styrene gives two epimers at C-4 of the lactone ring in the ratio 55 : 45.

Procedure for the Alkylation of Styrene by Di-n-octanoyl Peroxide.—A stock solution of copper(II) acetate, styrene, and peroxide was poured into a thermostatted (25 °C) and degassed 100 ml flask and solvent [CH_3COOH–CH_3CN (3 : 2)] was added to 49 ml. The magnetically stirred solution was flushed with nitrogen for 10 min, copper(I) acetate (1 ml) was added to start decomposition, and the reaction was run for 2 h under nitrogen at 25 °C.

Procedure for the Competitive Alkylation of Styrene and Acrylic Monomers.—The necessary amounts of acrylic monomer, styrene, copper(II) acetate and di-n-octanoyl peroxide were weighed in a 100 ml flask and solvent [CH_3COOH–CH_3CN (3 : 2)] was added to 49 ml. The degassed solution, magnetically stirred, was placed in a thermostatted bath and decomposition was initiated by adding 1 ml of the stock solution of copper(I) acetate. The reaction was run for 2 h at 25 °C.

Analysis.—Weighed amounts of oct-1-ene (99% by g.l.c.) and methyl laurilate ($C_9H_{19}CO_2Me$) (99% by g.l.c.) were added as internal standards to the reaction mixture. This solution (10 ml) was poured into water–pentane (30 ml; 2 : 1) at 0 °C, the pentane layer separated, and the water layer extracted with pentane (2 × 10 ml). The united pentane extracts were washed with water (10 ml), dried (Na_2SO_4) at 0 °C, and immediately analysed by g.l.c. on a 10% UCC column at 60 °C for hept-1-ene, n-heptane, and oct-1-ene. A portion was evaporated and analysed at 230 °C on the same column and on a 5% XE60 column for the alkylation products and for methyl laurilate.

The results for styrene, acrylonitrile, methyl acrylate, acrylic and methacrylic acid, and copper(II) acetate, are in Tables 1—5.

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