for the highly positive activation energy $(E_i)_{app}$ which is observed (~13 kcal mol^{-1}). This means that the above equilibrium is never reached and that the concentration of the solvated intermediate Ph_3C^+, M remains very low during the initiation. The apparent rate constant $(k_i)_{app}$ is then equal to k_2, which leads to a positive activation energy.

We could not decide between these two possible explanations but the effect of common ion salts is now being studied and might give us more information about the dissociation equilibrium of propagating species.

References and Notes

(1) P. M. Bowyer, A. Ledwith, and D. C. Sherrington, *Polymer,* **12,** 509 (1971).

(2) C. E. H. Bawn, C. Fitzsimmons, A. Ledwith, J. Penfold, D. C. Sherrington, and J. A. Weightman, *Polymer,* **12,** 119 (1971).

(3) A. Ledwith, E. Lockett, and D. C. Sherrington, *Polymer,* **16,** 31 (1975).

(4) Y. J. Chung, J. M. Rooney, D. R. Squire, and V. Stannett, *Polymer,* **16,** 527 (1975).

(5) G. Sauvet, J. P. Vairon, and P. Sigwalt, *Eur. Polym. J.,* **10,** 501 (1974).

(6) R. Cotrel, G. Sauvet, J. P. Vairon, and P. Sigwalt, Preprint C8-1, IIIrd International Symposium on Cationic Polymerization, Rouen, 1973.

(7) A. M. Goka and D. C. Sherrington, *Polymer,* **16,** 819 (1975).

(8) A. Sosa, *Ann. Chim. (Paris),* **14,** 89 (1940)

(9) W. M. Pasika, *J. Polym. Sci., Part A,* **3,** 4287 (1965).

(10) H. Cheradame, M. Mazza, N. A. Hung, and P. Sigwalt, *Eur. Polym. J.,* **9,** 375 (1973).

(11) H. Cheradame, J. P. Vairon, and P. Sigwalt, *Eur. Polym. J.,* **4,** 13 (1968).

(12) J. C. Favier, M. Fontanille, and P. Sigwalt, *Eur. Polym. J.,* **10,** 717 (1974).

(13) G. Sauvet, J. P. Vairon, and P. Sigwalt, *J. Polym. Sci., Part A-1,* **7,** 983 (1969).

(14) T. Higashimura, N. Kanoh, and S. Okamura, *J. Macromol. Sci., Chem.,* **1,** 109 (1966).

(15) P. M. Bowyer, A. Ledwith, and D. C. Sherrington, *J. Chem. Soc. B,* 1511 (1971).

(16) M. S. Sambhi and F. E. Treloar, *J. Polym. Sci., Polym. Lett. Ed.,* **3,** 445 (1965).

(17) T. Higashimura, T. Fukushima, and S. Okamura, *J. Macromol. Sci., Chem.,* **1,** 683 (1967).

(18) F. Subira, Thèse de spécialité, Université Pierre et Marie Curie, Paris, 1973.

(19) K. Yamamoto and T. Higashimura, *Polymer,* **16,** 815 (1975).

(20) K. Hayashi, K. Hayashi, and S. Okamura, *Polym. J.,* **4(3),** 426 (1973)

(21) C. M. Fontana and G. A. Kidder, *J. Am. Chem. Soc.,* **70,** 3745 (1948).

(22) P. Sigwalt, Plenary Lecture, IUPAC, Vol. IV, Boston, 1971, p 495.

(23) S. Slomkowski, P. Kubisa, and S. Penczcek, Preprints, Vol. 2, IUPAC International Symposium on Macromolecules, Helsinki, 1972, p 824; *J. Chem. Soc., Perkin Trans. 2,* 1718 (1974).

(24) G. Sauvet, J. P. Vairon, and P. Sigwalt, *J. Polym. Sci., Polym. Symp.,* **52,** 173 (1975).

Reactivity of Vinylferrocene and Vinylcymantrene in Radical Initiated Solution Copolymerizations

Charles U. Pittman, Jr.,* and Thane D. Rounsefell

Department of Chemistry, University of Alabama, University, Alabama 35486.

Received January 1, 1976

ABSTRACT: Vinylferrocene (M_1) has been classified within the *Q–e* scheme as an exceptionally electron rich vinyl monomer from copolymerization studies with 12 vinyl organic monomers. In copolymerizations with vinylcymantrene, *N*-vinylcarbazole, *p-N,N*-dimethylaminostyrene, 1,3-butadiene, *N*-vinyl-2-pyrrolidone, and styrene, the value of *e* for vinylferrocene was consistently in the range of −2.0 to −2.6 and the *Q–e* scheme was applicable. The *Q–e* scheme failed when electron deficient comonomers such as methyl methacrylate, methyl acrylate, acrylonitrile, diethyl fumarate, fumaronitrile, and maleic anhydride were employed, presumably due to competition of the charge transfer model with the terminal model. Vinylcymantrene exhibited the same copolymerization behavior and its value of *e* was about −2 when using electron-rich comonomers where the *Q–e* scheme held. The reactivity ratios, from which values of *e* were calculated, were obtained using the integrated form of the copolymer equation and the proper nonlinear least-squares fitting technique. The importance of this method, especially with regard to past classification of vinylferrocene by the *Q–e* scheme, is discussed.

Vinylferrocene, **1**, was first copolymerized with styrene, methyl acrylate, and chloroprene by Arimoto and Haven.[1] More recently, quantitative vinylferrocene copolymerization studies[2–8] have been carried in order to determine reactivity ratios and the values of *Q* and *e*[9] for this monomer. Similarly, quantitative copolymerization studies of vinylcymantrene, **2**, have recently been reported.[8,10] These studies are of fundamental interest in order to understand how organometallic functions effect vinyl polymerization behavior. This knowledge is needed to help design copolymers of vinyl organometallic monomers with classic organic monomers and also to provide a framework in which the electronic effects, that organometallic functions impart in radical initiated copolymerizations, may be viewed.

Reports of the value of *e* for vinylferrocene seem to be in disagreement in the literature. Using cationic initiation, a value of $e = -1.3$ was reported in styrene copolymerizations while values of about −2.1 and +0.47 have also been observed.[4,8,10,11] In this paper we report a careful classification of both vinylferrocene and vinylcymantrene according to the *Q–e* scheme. It is demonstrated that both monomers are exceptionally electron rich as indicated by their large negative values of *e*.

Results and Discussion

To evaluate the values of *Q* and *e*, the equation $r_1r_2 = \exp[-(e_1 - e_2)^2]$ is employed.[9] The values of r_1 and r_2 are first obtained by fitting experimental composition–conversion data to the copolymer equation.[9,12] The process of fitting this data should be performed by a *nonlinear* least-squares method.[12,13]

$$\frac{d[M_1]}{d[M_2]} = \left[\frac{[M_1{}^0]}{[M_2{}^0]}\right]\left[\frac{r_1[M_1{}^0] + [M_2{}^0]}{r_2[M_2{}^0] + [M_1{}^0]}\right]$$

Linear methods, such as the frequently used Fineman Ross technique,[14] are mathematically incorrect and in some cases lead to large errors.[13] Furthermore, the *integrated form* of the copolymer equation must be employed to account for monomer drift even when polymerizations to low conversions have been used.

Computer programs for routine application of the nonlinear least-squares fitting of the integrated form of the copolymer

Table I
Classification of Vinylferrocene (M_1) According to the *Q–e* Scheme in Copolymerizations with Organic Monomers

M_2	e_2	r_1	r_2	e_1 Calcd	Ref
Vinylcymantrene	−1.99	0.49	0.44	−2.6	9
N-Vinylcarbazole	−1.40	0.60	0.20	−2.4	4
p-*N*,*N*-Dimethylaminostyrene	−1.37	0.15	3.8	−2.2	This work
1,3-Butadiene	−1.05	0.3	3.5	−1.05	7[a]
	−1.05	0.14	3.97	−1.80	*b*
	−1.40[c]	0.14	3.97	−2.1	*b*, *c*
N-Vinyl-2-pyrrolidone	−0.90	0.67	0.33	−2.1	4
Styrene	−0.80	0.08	2.70	−2.04	3, 10
	−0.80	0.07	2.63	−2.1	3, 10[d]
	−0.80	0.2 ± 0.1	4 ± 1	−1.3	2
Methyl methacrylate	+0.40	0.52	1.22	−0.29	3
	+0.40	0.56	1.25	−0.20	3[d]
Methyl acrylate	+0.58	0.82	0.63	−0.21	3
	+0.58	0.73	0.61	−0.32	3[d]
Acrylonitrile	+1.20	0.15	0.16	−0.73	3[e]
	+1.20	0.11	0.17	−0.81	3[d]
Diethyl fumarate	+1.25	Alternating copolymer			6
Fumaronitrile	+1.96	Alternating copolymer			6
Maleic anhydride	+2.25	0.02 ± 0.04	0.19 ± 0.3	−0.11	5[f]

[a] Calculated from nine *nonoptimized* data points using the *differential* form of the copolymer equation using the incorrect *linear least-squares* fitting technique of Fineman and Ross. [b] Calculated using the same data from ref 7 using the *integrated form* of the copolymer equation where the values of r_1 and r_2 were fitted by the *nonlinear* least-squares method. [c] Values of −1.05 and −1.40 have been cited for the value of *e* for 1,3-butadiene. [d] Calculated using the same data of ref 3 and 10 using the *integrated form* of the copolymer eqution where r_1 and r_2 were fitted by the *nonlinear* least-squares method. [e] High tendency to alternation; $r_1 \cdot r_2 = 0.024$. [f] Alternating copolymer.

Table II
Classification of Vinylcymantrene (M_1) According to the *Q–e* Scheme in Copolymerizations with Organic Monomers[a]

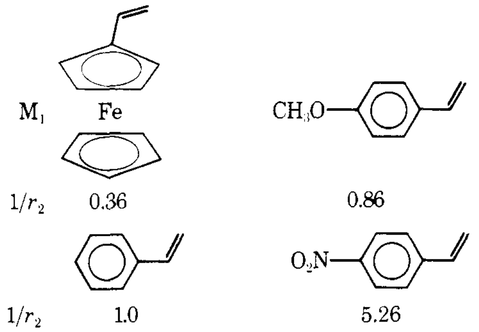
M_2	e_2	Solvent	r_1	r_2	e_1 Calcd	Ref
Vinylferrocene	−2.1	Benzene	0.44	0.49	−2.6	10
N-Vinyl-2-pyrrolidone	−0.90	Benzene	0.14	0.09	−2.9	8
Styrene	−0.80	Benzene	0.10	2.5	−2.0	10
Vinyl acetate	−0.22	Ethyl acetate	2.35	0.06	−1.62	10
Methyl acrylate	+0.58	Benzene	0.19	0.47	−0.95	10
Acrylonitrile	+1.20	Ethyl acetate	0.19	0.22	−0.59	10
Maleic anhydride	+2.25	Ethyl acetate	Alternating copolymer			This work

[a] All r_1 and r_2 values calculated from the integrated form of the copolymer equation employing the nonlinear least-squares fitting technique.

equation are available[12,13,15,16] which provide an objective mathematical criteria of confidence. However, in most cases where reactivity ratios have been determined, these "correct" techniques have not been employed. An additional consideration in determining reactivity ratios is that several copolymerization experiments should be carried out at the two *optimized* initial M_1^0/M_2^0 *feed ratios* in any determination of r_1 and r_2.[12,13] This has only been done in a few rare cases in the literature.[4,10,17,18] In the classification of monomers 1 and 2 in this paper, the reactivity ratios are obtained utilizing these important considerations.

Copolymerizations of vinylferrocene with a range of organic monomers, under conditions of AIBN radical initiation, are summarized in Table I. Electron-rich and electron-deficient comonomers were used. When electron-rich comonomers were used, vinylferrocene clearly fits the *Q–e* scheme. It is particularly striking that vinylferrocene exhibits one of the largest negative *e* values reported. In copolymerizations with vinylcymantrene, *N*-vinylcarbazole, *p*-*N*,*N*-dimethylaminostyrene, butadiene, *N*-vinyl-2-pyrrolidone, and styrene the value of *e* for vinylferrocene was between −2.6 and −2.0. For extensive styrene copolymerizations, *e* = −2.1 for vinylferrocene. In all cases, the *integrated form* of the copolymer equation was solved employing the *nonlinear* least-squares fitting method. In all cases except where M_2 was 1,3-butadiene (or styrene in cationic copolymerizations), several experiments at the *optimized feed ratios* were also performed. Thus, it is now believed that the "best" value of *e* for vinylferrocene is between −2.0 and −2.6 and is probably about −2.1.

That vinylferrocene is an exceptionally electron-rich monomer in free radical copolymerizations can be emphasized, further, by examining the values of $1/r_2$ in the following series of copolymerizations. In each case M_2 is styrene.



Compared to a phenyl group, ferrocene exhibits an extraordinary ability to stabilize adjacent positive charge.[19–21] For example, the value of σ^+ for *p*-ferrocene is −0.71 and for

α-ferrocenyl groups it is -1.4.[19] Available evidence suggests that ferrocenyl substituents destabilize radical anions[22] and radicals[23,24] relative to the effect of a phenyl ring.

The second striking feature in Table I is that the Q–e scheme breaks down when M_2 is an electron deficient monomer. This phenomena is somewhat like a sudden change in the slope of a Hammett σ–p plot. It strongly suggests that a change in polymerization mechanism has occurred. Since the Q–e scheme is defined in terms of the terminal copolymerization model,[9] when another mechanism operates, the Q–e scheme is no longer appropriate to apply and has no meaning. For example, if a fraction of the monomer units entering the copolymer were incorporated as charge-transfer complexes, then the Q–e scheme would no longer apply because the charge-transfer model would be operating in competition with the terminal model.

Where M_2 is methyl methacrylate, methyl acrylate, and acrylonitrile, we suspect that both terminal and charge-transfer processes occur in competition. Where M_2 is diethyl fumarate, fumaronitrile, or maleic anhydride, alternating copolymers are obtained and evidence for the operation of the charge-transfer model has been presented.[6] When reviewed in the context of all 12 comonomers shown in Table I, this explanation explains logically the success of the Q–e scheme with electron-rich monomers and the failure of the scheme with electron-deficient monomers.

A similar classification is apparent when vinylcymantrene is copolymerized with vinyl monomers covering a wide range of e values. Table II summarizes the available data where all r_1 and r_2 values have been calculated using the integrated form of the polymer equation and the nonlinear least-squares fitting technique. Like vinylferrocene, vinylcymantrene is shown to have an exceptionally large negative value of e (-2.6 to -1.62). When M_2 is styrene, $e = -2.0$. Thus, to a first approximation, the values of e for vinylferrocene and vinylcymantrene are about the same.

When electron-deficient comonomers (methyl acrylate, acrylonitrile, maleic anhydride) were used, the Q–e scheme fails. This further illustrates the parallel in behavior of vinylcymantrene and vinylferrocene. It is interesting that the electronic effects of electron-withdrawing carbonyl groups on manganese are not manifest at the vinyl group. The effect of the electron-rich cyclopentadienyl ring dominates electronic effects in the vinyl groups of both **1** and **2**.

Finally, the importance of using (a) the integrated form of the copolymer equation and (b) fitting r_1 and r_2 to experimental results using the nonlinear least-squares method is illustrated for vinylferrocene–butadiene copolymerizations in Table I.[26] George and Hayes[7] reported nine copolymerization experiments to "fairly low" conversions (the highest was 14%). Using the differential form of the copolymer equation and the linear Fineman Ross fitting method, they calculated $r_1 = 0.3$, $r_2 = 3.5$, and $e_1 = -1.05$ (vinylferrocene $= M_1$). When their data are recomputed using the integrated form of the copolymer equation and the nonlinear fitting method, $r_1 = 0.14$, $r_2 = 3.97$, and $e_1 = -1.8$ (or -2.1 if a value of -1.40 is chosen for e_2). Thus, butadiene copolymerizations do not lead to an anomalously low value of e for vinylferrocene based on the data now available. Clearly, proper treatment of available data is quite important when dealing with the Q–e scheme.

Acknowledgments. Support of this work by the Office of Naval Research and by the Materials Science Division of the National Science Foundation, Grant No. DMR73-07545-A01, is gratefully acknowledged.

References and Notes

(1) F. S. Arimoto and A. C. Haven, Jr., *J. Am. Chem. Soc.*, **77**, 6295 (1955).
(2) C. Aso, T. Kunitake, and T. Nakashima, *Kogyo Kagaku Zasshi*, **72 (6)**, 1411 (1969).
(3) J. C. Lai, T. D. Rounsefell, and C. U. Pittman, Jr., *J. Polym. Sci., Part A-1*, **9**, 651 (1971).
(4) C. U. Pittman, Jr., and P. L. Grube, *J. Appl. Polym. Sci.*, **18**, 2269 (1974).
(5) C. U. Pittman, Jr., R. L. Voges, and J. Elder, *J. Polym. Sci., Part B*, **9**, 191 (1971).
(6) K. Tada, H. Higuchi, M. Yoshimura, H. Mikawa, and Y. Shirota, *J. Polym. Sci., Polym. Chem. Ed.*, **13**, 1737 (1975).
(7) M. H. George and G. F. Hayes, *Makromol. Chem.*, **177**, 399 (1976).
(8) C. U. Pittman, Jr., and P. L. Grube, *J. Polym. Sci., Part A-1*, **9**, 3175 (1971).
(9) For a review, see T. Alfrey, Jr., J. J. Bohrer, and H. Mark, "Copolymerization", Vol. III, Interscience, New York, N. Y., 1952.
(10) C. U. Pittman, Jr., G. V. Marlin, and T. D. Rounsefell, *Macromolecules*, **6**, 1 (1973).
(11) The positive value of e was inadvertently reported in ref 4 despite the fact that data also give a value of $e = -2$ for the negative solution of the Price equation.[8]
(12) P. W. Tidwell and G. A. Mortimer, *J. Polym. Sci., Part A-1*, **3**, 369 (1965).
(13) P. W. Tidwell and G.A. Mortimer, *J. Macromol. Sci., Rev. Macromol. Chem.*, **4**, 281 (1970).
(14) M. Fineman and S. D. Ross, *J. Polym. Sci.*, **5**, 259 (1950).
(15) C. U. Pittman, Jr., and T. D. Rounsefell, *Macromolecules*, **8**, 46 (1975).
(16) C. U. Pittman, Jr., and T. D. Rounsefell, *J. Polym. Sci., Polym. Chem. Ed.*, **11**, 621 (1973).
(17) C. U. Pittman, Jr., O. E. Ayers, and S. P. McManus, *Macromolecules*, **7**, 737 (1974).
(18) S. P. McManus, W. J. Patterson, and C. U. Pittman, Jr., *J. Polym. Sci., Polym. Chem. Ed.*, **13**, 1721 (1975).
(19) T. G. Traylor and J. C. Ware, *J. Am. Chem. Soc.*, **89**, 2304 (1967).
(20) M. Cais, *Organomet. Chem. Rev.*, **1**, 435 (1966).
(21) C. U. Pittman, Jr., *Tetrahedron Lett.*, **37**, 3619 (1967).
(22) C. Elschenborvich and M. Cais, *J. Organomet. Chem.*, **18**, 135 (1969).
(23) A. A. Berlin, *Khim. Promst. (Kiev)*, 881 (1962).
(24) E. G. Perevalova and Yu. A. Ustynayak, *Izv. Akad. Nauk SSSR*, 1776 (1973).
(25) J. Seiner and M. Litt, *Macromolecules*, **4**, 308, 312, 314, 316 (1971).
(26) The data in Tables I and II were computed from experimental data cited in the references of those tables. For most cases a large number of copolymerization experiments were available.