McCrone interpretation, must add additional weight to the conclusion that the Vinland Map is a painstakingly clever forgery.

The microchemical evidence is equally difficult to place in context with the Map's authenticity:

How could a genuine 15th century document have been drawn with an ink containing particles that are mineralogically and crystallographically indistinguishable from a modern paint pigment whose manufacture requires specific and sequential technological procedures?

If pigment-quality anatase had been unknowingly or accidentally added to the Map's surface at some later date, how could titanium be enriched on the inked lines and lettering throughout the Map, but not appear, above background, on the parchment itself?

With all of the chemical, microscopical, historical, and cartographic data now available, it is increasingly difficult to argue that the Vinland Map could still be an authentic 15th century document. If further research is to be devoted to this document and its provenance, perhaps it should be addressed toward an attempt to identify the forger(s), the source(s) of the inks, and the motives for its forgery.

I thank T. A. Cahill, K. D. Harrington, W. A. Kampfer, Walter C. McCrone, Lucy McCrone, and J. S. Olin. The referees provided useful suggestions for improvement of the manuscript.

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Bromonium Ions or β-Bromocarbocations in Olefin Bromination. A Kinetic Approach to Product Selectivities

MARIE-FRANÇOISE RUASSE

Institut de Topologie et de Dynamique des Systèmes de l'Université Paris 7, associé au CNRS, 1, rue Guy de la Brosse, 75005 Paris, France

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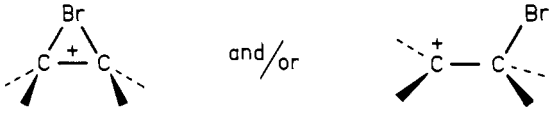
The bromonium ion, first proposed in 1937 by Roberts et al. to interpret the stereoselective bromination of 2-butenes,[1] is a classic example of a bridged ionic intermediate. Although its existence in textbooks appears to be long-established, bromine bridging in transition states and intermediates was not demonstrated until 30 years later. Moreover, as proof of the occurrence of bromonium ions was accumulating, evidence for open transition states and intermediates in olefin bromination was also found.[2] This Account aims to explain how bromine bridging depends on the olefin structure and on the solvent.



The first conclusive stereochemical proof of halogen bridging in halogenation intermediates was established in 1966 by the elegant work of Fahey et al. on the chlorination of *cis*- and *trans*-1,2-di-*tert*-butylethylenes,[3] found to be 100% stereoselective.[4] Chlorination of the cis olefin leading to an exceptionally strained bridged ion goes through a chloronium ion; a fortiori, bromination must go through a bromonium ion since bromine is a better bridging group than chlorine. Surprisingly, bromine bridging was shown to occur as early as 1948 in solvolysis,[5] but not until 1978 did rate data on alkene bromination reveal[6] that the charge distribution is symmetrical in the late transition state, which implies bromine bridging in the intermediate.

Evidence for open carbocationic transition states and intermediates was also advanced in the 1960s. *cis*-Anetholes and *trans*-anetholes, 4-$MeOC_6H_4CH{=}CHMe$, are brominated with the same lack of stereoselectivity.[7] The ρ^+ value of the $\rho^+\sigma^+$ correlation of styrene bromination rates in methanol[8] and acetic acid[9] closely resembles that of *tert*-cumyl chloride methanolysis. The first qualitative interpretation of the 2-fold nature of these ions was contained in Yates's proposal that there was a spectrum of intermediates going from bromonium ions to β-bromocarbocations.[10] Our own more quantitative analysis is based on rate–product relationships, which are capable of predicting bromination selectivities.

Marie-Françoise Ruasse is a native of Paris, France. She attended the Faculty of Sciences of Paris at the Sorbonne and received her Doctorat es Sciences in 1965 for work on synthesis of gallic acid derivatives. She moved to Physical Organic Chemistry in Professor Dubois's group in 1966 and is now a CNRS Research Director. Current research interests are in the area of reaction mechanisms and, in particular, the role of the solvent in determining reactivity and selectivity.

(1) Roberts, I.; Kimball, G. E. *J. Am. Chem. Soc.* **1937**, *59*, 947.
(2) (a) Freeman, F. *Chem. Rev.* **1975**, *75*, 441. (b) Schmid, G. H.; Garrat, D. G. *Double Bonded Functional Groups*; Patai, S., Ed.; Wiley: New York, 1977; Suppl. A, p 725. (c) de la Mare, P. B. D.; Bolton, R. *Electrophilic Additions to Unsaturated Systems*, 2nd ed.; Elsevier: Oxford, 1982.
(3) (a) Fahey, R. C. *J. Am. Chem. Soc.* **1966**, *88*, 4681. (b) Fahey, R. C. *Topics in Stereochemistry*; Eliel, E. L., Allinger, N. L., Eds.; Interscience Pub.: New York, 1968; Vol. 3, p 237; (c) When rearrangement occurs in alkene bromination, rearranged products arise from a bridged bromonium ion and not from an open cation, as shown in the examples of *trans*-1,2-di-*tert*-butylethylene[3a] and norbornene.[3b]
(4) For definitions, see: Glossary of Terms Used in Physical Organic Chemistry. *Pure Appl. Chem.* **1983**, *55*, 1281.
(5) Winstein, S.; Grunwald, E.; Ingraham, L. L. *J. Am. Chem. Soc.* **1948**, *70*, 821. Grunwald, E. *Ibid.* **1951**, *73*, 5458.
(6) Bienvenue-Goetz, E.; Dubois, J. E. *Tetrahedron* **1978**, *34*, 2021.
(7) Fahey, R. C.; Schneider, H. J. *J. Am. Chem. Soc.* **1968**, *90*, 4429.
(8) Dubois, J. E.; Schwarcz, A. *Tetrahedron Lett.* **1964**, 2167.
(9) Rolston, J. H.; Yates, K. *J. Am. Chem. Soc.* **1969**, *91*, 1483.
(10) Yates, K.; McDonald, R. S. *J. Org. Chem.* **1973**, *38*, 2465.

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How Product Selectivities Are Related to Bridging in the Intermediates

Bromination exhibits three types of selectivity for product formation in nucleophilic solvents, but none of them alone are enough to establish the structure of the ionic intermediate.

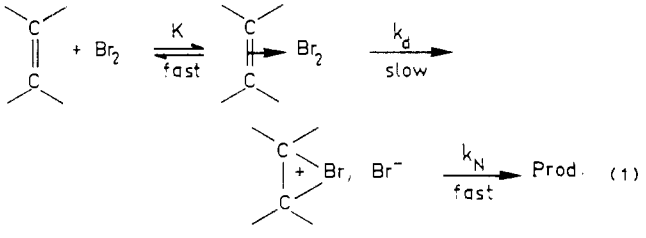
Stereoselectivity depends on bromine bridging; it is 100% anti for a bromonium ion[3c] and less than this for carbocations. The lower limit is known only when the reaction of two cis–trans isomeric olefins leads to the same stereochemical outcome, as, for example, in the case of the anetholes.[7]

Regioselectivity for solvent-incorporated products depends on the relative charges borne by the two carbon atoms of the intermediates.[11] For carbocations, bromination must be 100% regioselective, but for bromonium ions, the charge distribution is less straightforward. The orientation of nucleophile addition is expected to follow Markovnikov's rule, but more quantitative predictions are difficult.

Chemoselectivity between two nucleophiles, generally the bromide ion and a nucleophilic solvent, depends on their relative nucleophilicities and also on the electrophilicity of the ionic intermediate. Extensive data on chemoselectivity are available only for the competition between the bromide ion and acetic acid[12] or methanol.[11] Some empirical rules have been deduced: (i) more solvent-incorporated product is formed from carbocations than from bromonium ions and (ii) methanol competes with bromide ions more efficiently than acetic acid. However, this simple picture may not hold if steric effects and ion pairing arise. Chemoselectivity is not in itself compelling evidence for one sort of ion or another but may be adduced as confirmation of conclusions based on the other two selectivities.

How Rates Are Related to the Structure of the Intermediates

In protic solvents, such as water, methanol, or acetic acid, free bromine addition to olefins is believed to follow the Ad_EC1 mechanism where σ- and π-complexes are formed successively in two separate steps.[13] In



aprotic solvents, an analogous mechanism is postulated.[14] The dissociation of the olefin–bromine charge-transfer complex (CTC) is assisted by the solvent in protic media[15] and by a second bromine in nonprotic media.[16]

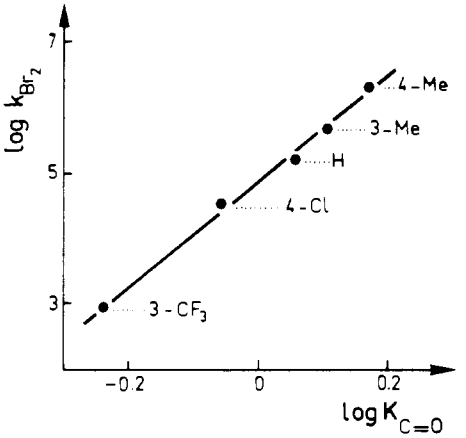


Figure 1. Comparison of ring-substituent effects on the bromination rates of α-methylstyrenes and on equilibrium constants of the formation of the iodine–acetophenone CTCs (data from refs 18 and 35). The contribution of the olefin–bromine CTC formation to the substituent effects on bromination rates cannot be greater than 9% (iodine is a better acceptor than bromine and ketone a better donor than olefins: therefore, $\rho_K < 0.1\ \rho_d$).

The first step of the Ad_EC1 mechanism is the fast, reversible formation of a *bromine–olefin charge-transfer complex*.[17] This preequilibrium would tend to reduce the information content of the experimental rate constant regarding the intermediate structure, since k is related to the formation of the ionic intermediate *and* to that of the CTC, $k = Kk_d$. However, since the substituent or solvent effects on K are probably much smaller than those on k_d, ρ or m values in structure–reactivity or solvent–reactivity correlations based on k should be closely similar to those of the ionization process. This assumption is supported by the fact that the charge development is small in the first step but large in the second.[17b] This is inferred from the small solvent dependence[17c] of the equilibrium constant for the cyclohexene–bromine CTC and from the large value of the slope of Figure 1, which compares substituent effects on α-methylstyrene bromination and on acetophenone–iodine CTC formation.[18]

According to eq 1, the *rate-determining step* leads to the ionic intermediate by unimolecular[19] dissociation of the CTC. The existence of such intermediates and their occurrence in bromination are supported by a mass of evidence based on (i) product formation (vide supra); (ii) spectroscopic observations;[20] (iii) theoretical

(11) Dubois, J. E.; Chrêtien, J. R. *J. Am. Chem. Soc.* **1978**, *100*, 3506.
(12) Rolston, J. H.; Yates, K. *J. Am. Chem. Soc.* **1969**, *91*, 1469.
(13) (a) Garnier, F.; Dubois, J. E. *Bull. Soc. Chim. Fr.* **1968**, 3797. (b) Olah, G. A.; Bollinger, J. M. *J. Am. Chem. Soc.* **1968**, *90*, 6082. Olah, G. A.; Hockswender, T. R., Jr. *Ibid.* **1974**, *96*, 3574.
(14) Buckles, R. E.; Miller, J. L.; Thurmaier, R. J. *J. Org. Chem.* **1967**, *32*, 888. de la Mare, P. B. D.; Wilson, K. D. *J. Chem. Soc., Perkin Trans. 2* **1977**, 2048.
(15) Garnier, F.; Donnay, R.; Dubois, J. E. *J. Chem. Soc. D* **1971**, 829.
(16) Bellucci, G.; Berti, G.; Bianchini, R.; Ingrosso, G.; Yates, K. *J. Org. Chem.* **1981**, *46*, 2315.
(17) (a) Dubois, J. E.; Garnier, F. *Spectrochim. Acta, Part A* **1967**, *23A*, 2279. (b) Recently Bellucci et al. (Bellucci, G.; Bianchini, R.; Chiappe, C.; Marioni, F.; Ambrosetti, R.; Brown, R. S.; Slebocka-Tilk, H. *J. Am. Chem. Soc.* **1989**, *111*, 2640) claimed that the substituted dependence of K could be large because the formation constant (290 M^{-1}) of the adamantylideneadamantane–bromine CTC complex is much higher than that[17c] (0.5 M^{-1}) of the cyclohexene complex. It can, however, be argued that the adamantylideneadamantane reaction is an atypical bromination.[23] Moreover, as shown in Figure 1, the relative importance of the substituent effects on the two first bromination steps can only be estimated by comparing the CTC formation constants and the bromination rate constants, unknown for adamantylideneadamantane. (c) Bellucci, G.; Bianchini, R.; Ambrosetti, R. *J. Am. Chem. Soc.* **1985**, *107*, 2464 and references therein.
(18) Laurence, C.; Guiheuneuf, G.; Wojtkowiak, B. *J. Am. Chem. Soc.* **1979**, *101*, 4793.
(19) Since bromonium ions are not formed from bromine and olefins in the gas phase (Angelini, G.; Speranza, M. *J. Am. Chem. Soc.* **1981**, *103*, 3792), the solvent must strongly assist the ionization of the CTC. Most of the assistance comes from the electrophilic solvation of the leaving bromide,[15] but nucleophilic solvent participation has also been detected. Ruasse, M. F.; Zhang, B. L. *J. Org. Chem.* **1984**, *49*, 3207. Ruasse, M. F.; Lefebvre, E. *Ibid.* **1984**, *49*, 3210. Ruasse, M. F.; Motallebi, S. *Bull. Soc. Chim. Fr.* **1988**, 349.

Table I
ρ Values[a] for Substituent Effects in Methanol and m Values for Solvent Effects in Olefin Bromination via the Multipathway Mechanism

olefin	pathways: bromonium	pathways: carbocations C_α	pathways: carbocations C_β	m^b
alkenes[c]	−3.1 (σ^*)			1.1–1.3[d]
styrenes[e]	−3.7 (σ)	−4.8 (σ^+)		0.96[f]
trans-β-methylstyrenes[e]	−3.7 (σ)	−4.7 (σ^+)		
α-methylstyrenes[e]		−4.3 (σ^+)[g]		0.97[d]
stilbenes[h]	−1.0 (σ)	−5.4 (σ^+)	−1.6 (σ)	1.20[f]
α-methylstilbenes[i]		−4.6 (σ^+)[g]	−1.7 (σ)	1.04[j]
		−5.0 (σ^+)[g]	−2.1 (σ)	
1,1-diphenylethylenes[k]		−3.6 (σ^+)[g]		1.00[j]

[a] The σ scale used is given in parentheses. [b] Calculated by using Winstein–Grunwald Y values. [c] Reference 26b. [d] Reference 19. [e] These values are those obtained by the iterative procedure (see text). Data from ref 35. [f] Reference 22c. [g] $\sigma^+ = \sigma + r_{Y\text{-}T}\Delta\sigma^+$. [h] Iterative procedure. Data from ref 30. [i] Reference 36. [j] Unpublished results. [k] Reference 42.

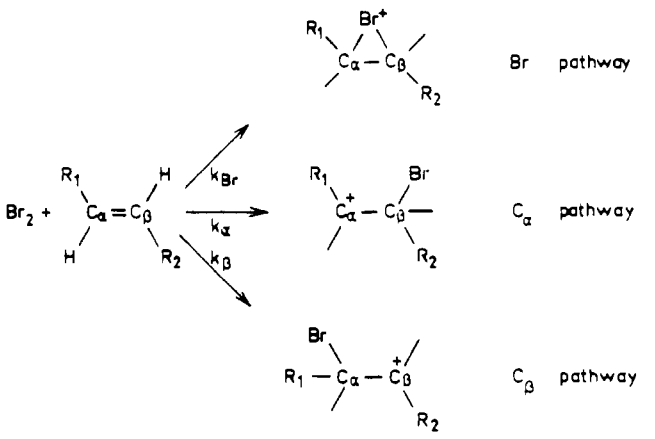
calculations;[21] and (iv) kinetic measurements which show high sensitivities to solvent and substituent change, analogous to those observed in S_N1 reactions.[13a,22]

It is well-established, mainly by solvent effects, that for most olefins in protic solvents, *the ionic intermediate is formed irreversibly*.[23] Linear Winstein–Grunwald relationships have been reported[13a,22] for a large variety of solvents, with m values generally higher than 1. The rates measured by following bromine uptake are, therefore, ionization rates. The common and noncommon salt effects[25] are not readily interpreted in terms of ion pairing and eventual return since the competition between the addition of free bromine and that of the electrophilic tribromide ion (eq 2) obscures the meaning of the salt-effect coefficients. Bromide ion effects follow eq 3, first proposed by Bartlett et al.[26]

$$Br_2 + Br^- \rightleftharpoons Br_3^- \qquad (2)$$

$$k_{exptl}(1 + K[Br^-]) = \alpha + \beta[Br^-] \qquad (3)$$

Scheme I



The α term is the rate constant k for free bromine addition, readily obtained by extrapolating eq 3 to zero bromide ion concentration. The β term is to be related to tribromide ion addition, $k_{Br_3^-}$, to the usual salt-effect coefficient and to the rate constant of an eventual bromide-assisted bromine addition.[26] Because of this complexity, structure–reactivity or solvent–reactivity correlations have been based on the constants k corresponding to the free bromine addition only. Since products are not formed by this mechanism only, the use of k instead of k_{exptl} in rate–product relationships could be misleading. However, this has not proved to be an obstacle, probably because fairly good correlations between log k and log k_{exptl} with slopes close to 1 are found,[27] e.g., for substituted alkylethylenes in methanol.[28]

$$\log k = 1.04 \log k_{exptl} + 1.06 \qquad (4)$$

Finally, if the bromination rate is to furnish information about the structure of the ionic intermediate, the rate-determining transition state must closely resemble the intermediate. This has been shown by kinetic solvent effects: (i) the m values of the Winstein–Grunwald equations are close to 1 (Table I), indicating highly charged and, therefore, late transition states; (ii) solvent isotope effects (about 1.3 in AcOH and 1.4 in methanol) are large;[29] and (iii) there is a linear relationship (slope = 0.9) between the transfer energies of a bromide ion and the bromination rates.[15]

The Multipathway Scheme

As a working hypothesis we proposed[30] that bromonium and β-bromocarbocations could be formed in electrophilic bromination by discrete pathways according to Scheme I. In limiting cases, only one

(20) (a) Olah, G. A.; Bollinger, J. M. *J. Am. Chem. Soc.* **1968**, *90*, 947. (b) Olah, G. A.; Westerman, P. W.; Melby, E. G.; Mo, Y. K. *Ibid.* **1974**, *96*, 3565. (c) Olah, G. A. *Halonium Ions*; Wiley: New York, 1975. (d) McManus, S. P.; Peterson, P. E. *Tetrahedron Lett.* **1975**, 2753. (e) McManus, S. P.; Worley, S. D. *Ibid.* **1977**, 555. (f) Slebocka-Tilk, H.; Ball, R. G.; Brown, R. S. *J. Am. Chem. Soc.* **1985**, *107*, 4504.

(21) Bach, R. D.; Henneike, H. F. *J. Am. Chem. Soc.* **1970**, *92*, 5589. Hehre, W. J.; Hiberty, P. C. *Ibid.* **1974**, *96*, 2665. Poirier, R. A.; Mezey, P. G.; Yates, K.; Csizmadia, I. G. *J. Mol. Struct.: THEOCHEM* **1981**, *85*, 153. Poirier, R. A.; Demaré, G. R.; Yates, K.; Csizmadia, I. G. *Ibid.* **1983**, *94*, 137. Yamabe, S.; Minato, T.; Inagaki, S. *J. Chem. Soc., Chem. Commun.* **1988**, 532.

(22) (a) Bienvenue-Goetz, E.; Dubois, J. E. *Tetrahedron* **1968**, *24*, 6777. (b) Barbier, G.; Dubois, J. E. *J. Chim. Phys. Phys.-Chim. Biol.* **1968**, *65*, 1989. (c) Ruasse, M. F.; Dubois, J. E. *J. Am. Chem. Soc.* **1975**, *97*, 1977.

(23) Reversible formation of bromonium ions postulates that nucleophilic attack in the last product-forming step is slow. In protic solvents where nucleophiles are always present, this is generally not the case. However, crowding of the double bond can slow the last step by sterically inhibiting the reaction of the nucleophiles with the intermediate, as, for example, in the anomalous bromination of adamantylideneadamantane (Strating, J.; Wieringa, J. H.; Winberg, H. *J. Chem. Soc., Chem. Commun.* **1969**, 907). In nonnucleophilic aprotic solvents, the nucleophilic bromide ion is supplied by the dissociation of the tribromide counterion, which is not necessarily fast (Ruasse, M. F.; Aubard, J.; Galland, B.; Adenier, A. *J. Phys. Chem.* **1986**, *90*, 4382). In these latter solvents, some evidence for reversible formation of bromonium ions has been recently found in more or less drastic conditions.[24]

(24) Brown, R. S.; Gedye, R.; Slebocka-Tilk, H.; Buschek, J. M.; Kopecki, K. *J. Am. Chem. Soc.* **1984**, *106*, 4515. Bellucci, G.; Chiappe, C.; Marioni, F. *Ibid.* **1987**, *109*, 515. Bellucci, G.; Marioni, F.; Spagna, R. *Ibid.* **1988**, *110*, 546.

(25) Huynh, X. Q.; Dubois, J. E. *J. Chim. Phys. Phys.-Chim. Biol.* **1972**, *69*, 1482, 1488.

(26) (a) Bartlett, P. D.; Tarbell, D. S. *J. Am. Chem. Soc.* **1936**, *58*, 466. (b) Dubois, J. E.; Bienvenue-Goetz, E. *Bull. Soc. Chim. Fr.* **1968**, 2089. (c) Dubois, J. E.; Huynh, X. Q. *Tetrahedron Lett.* **1971**, 3369. To the best of our knowledge, only two olefins, tri-*tert*-butylethylene (Dubois, J. E.; Loizos, M. *C. R. Seances Acad. Sci., Ser. C* **1972**, *274*, 1130) and 2-acetoxy-2-cholestene (Calvet, A.; Josefowicz, M.; Levisalles, J. *Tetrahedron* **1983**, *39*, 103) do not follow eq 3. In these cases, the observed bromide ion effects are consistent with but do not prove reversible formation of the bromonium ions.

(27) Dubois, J. E.;Huynh, X. Q. *Bull. Soc. Chim. Fr.* **1968**, 1436.

(28) Thirty-seven alkenes; $0.67 < \log k < 7.14$; statistical coefficients: $R = 0.997$, $s_{slope} = 0.012$ (Ruasse, M. F.; Argile, A.; Bienvenue-Goetz, E.; Dubois, J. E. *J. Org. Chem.* **1979**, *44*, 2758).

(29) Modro, A.; Schmid, G. H.; Yates, K. *J. Org. Chem.* **1979**, *44*, 4221.

(30) (a) Ruasse, M. F.; Dubois, J. E. *J. Org. Chem.* **1972**, *37*, 1770. (b) Ruasse, M. F.; Dubois, J. E. *Ibid.* **1973**, *38*, 493. (c) Ruasse, M. F.; Dubois, J. E. *Ibid.* **1974**, *39*, 2441.

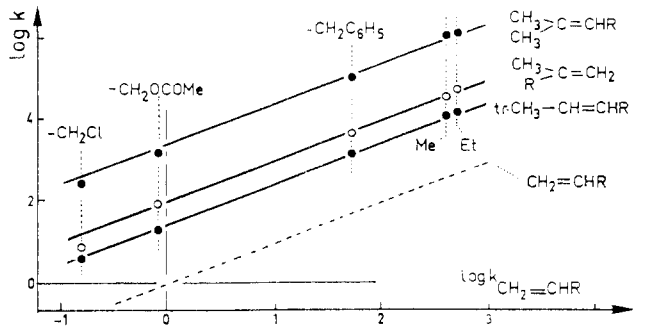


Figure 2. Comparison of the effect of a substituent R on the bromination rate of ethylene (abscissa) and of methylethylenes (ordinate). The dashed line is the first bisector; the four lines are parallel. The effect of R does not depend on its position, trans or geminate, with respect to a methyl group. This implies bromonium-like transition states (data from ref 6).

pathway, either C_α or Br for example, is followed; in intermediate situations, the degree of bromine bridging is given by the relative rates of formation of the carbocations and the bromonium ion. In the C_α and C_β pathways, the effect of R_1 must be greater or smaller, respectively, than that of R_2 whereas, in the Br path, both substituents must influence the rate to the same small extent. Substituent effects are, therefore, appropriate tools for separating out the elementary constants from the overall rates (eq 5). Consequently,

$$k = k_\alpha + k_\beta + k_{Br} \quad (5)$$

predicting selectivities from the rates boils down to measuring the parameters of the $\rho\sigma$ relationships for every pathway. The multipathway scheme should give nonlinear free energy relationships for substituent effects. Since the free energy relationship for the overall rates (associating eqs 5 and 6 gives a sum of exponential terms) has no straightforward mathematical solution, the curved FERs must be analyzed empirically either by adjusting experimental and calculated values iteratively or by seeking limiting situations. Both procedures have been used.

$$\log (k_\alpha/k_{0\alpha}) = \rho_\alpha\sigma_{R_1} + \rho_\beta\sigma'_{R_2}$$

$$\log (k_\beta/k_{0\beta}) = \rho_\alpha\sigma_{R_2} + \rho_\beta\sigma'_{R_1}$$

$$\log (k_{Br}/k_{0Br}) = \rho_{Br}(\sigma'_{R_1} + \sigma'_{R_2}) \quad (6)$$

Bromonium Transition States and Intermediates in Alkene Bromination

The first $\rho^*\sigma^*$ relationship[31] for alkene bromination included mono-, di-, and trisubstituted alkenes; polar effects were shown to be additive whatever the relative positions of the substituents. This was the first argument for a symmetric charge distribution, i.e., for a bromonium ion like transition state. However, correlation 7 is limited to straight-chain alkyl groups; the

$$\log k = -3.10\sum\sigma^* + 7.02 \quad (7)$$

inclusion of branched substituents causes scatter which is not eliminated by expressing the data in terms of an extended Taft–Ingold relationship, $\log k/k_0 = \rho^*\sum\sigma^* + \delta\sum E_s$. An attempt to correlate alkene rates by FER for the multipathway scheme provides a statistically significant but chemically meaningless description.[6,32]

(31) Mouvier, G.; Dubois, J. E. *Bull. Soc. Chim. Fr.* **1968**, 1441.

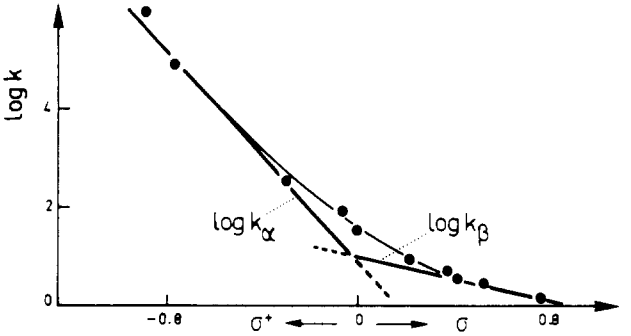
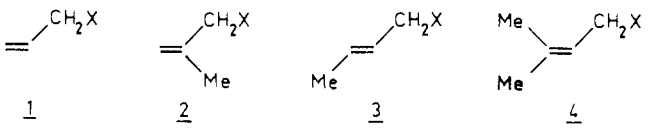


Figure 3. The curved $\rho\sigma$ plot in the bromination of monosubstituted stilbenes in methanol (data from ref 30). There is a mechanistic change when the substituent goes from strongly electron donating to strongly electron withdrawing.

The most clear-cut evidence for bromonium transition states is given by the polar effects of various small heteroatomic substitutents on methyl-substituted olefins.[6] Figure 2 shows that the influence of X does not depend on its position, trans or geminate, relative to a methyl group; consequently, the transition-state charge is essentially on the bromine.



1 2 3 4

Kinetic[6] and stereochemical[3] data support complete bromine bridging in both transition states and intermediates. However, there are some noticeable discrepancies between the two species:[33a] kinetics (Figure 2) indicates a symmetric charge distribution in the transition states, whereas regiochemical[33b] and spectroscopic[20] results on bromonium ions derived from gem-disubstituted alkenes imply that it is dissymmetric. These differences are not still fully understood.

Competition between Carbocations and Bromonium Ions in Aryl Olefin Bromination

The first stereochemical evidence for a partially bridged intermediate was found[34] in the *stilbene series*; furthermore, the multipathway mechanism was first proposed[30] to account for the kinetics of stilbene bromination where, depending on the aryl substituents, the *three pathways can compete*. The structure–reactivity relationship for the reaction of monosubstituted stilbenes[30a] gives a markedly curved $\rho\sigma$ plot, with obvious asymptotes (Figure 3). There is unambiguously competition between at least two pathways. Kinetic study of X,Y-disubstituted stilbenes with one electron-donating group shows[30b] that the effects of two substituents on each of the two aromatic rings are not additive, which suggests a highly dissymmetric charge distribu-

(32) Bergmann, H. J.; Collin, G.; Just, G.; Müller-Hagen, G.; Pritzkow, W. *J. Prakt. Chem.* **1972**, *314*, 285.

(33) (a) A variation in the magnitude of bridging on going from rate- to product-determining transition states has been postulated.[2b] However, since the first transition state is late and the product formation fast, according to the Hammond postulate (Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334) both transition states should closely resemble the intermediate. It is, therefore, unexpected that bromine bridging is significantly modified along this highly energetic part of the chemical pathway. (b) The reaction of the *gem*-R,R′-alkenes (R = Me, R′ = Me, Et, *i*-Pr, *neo*-Pe and *tert*-butyl) is 100% regioselective, nucleophilic solvent attacking only the most substituted carbon of the bromonium ion. (Chrétien, J. R., unpublished results and ref 11.)

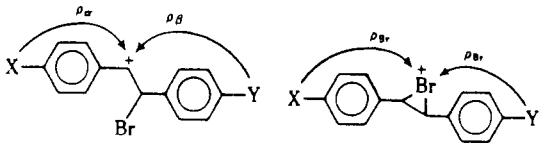
(34) (a) Heublein, G. *J. Prakt. Chem.* **1966**, *303*, 84. (b) Buckles, R. E.; Bader, J. M.; Thurmaier, R. J. *J. Org. Chem.* **1962**, *27*, 4523.

Table II
Bromination of Stilbenes in Methanol. Comparison of the Experimental Rates, of the Rates Calculated by the Three-Pathway Mechanism, and of the Regiochemistry

X[a]	Y[a]	log k[b]	predominant paths[c] C_α	C_β	Br	% MeOH attack on C_α[d]
4-OH	4-OMe	5.97 (5.73)	+	+		
4-Me	H	1.88 (1.91)	+	+		97 (95)
H	H	1.04 (0.56)	+	+	+	50 (50)
4-Cl	H	0.29 (0.11)	+	+	+	34 (35)
3-CF_3	H	−0.07 (−0.31)		+	+	0 (0)
4-NO_2	3-Cl	−1.57 (−1.58)			+	

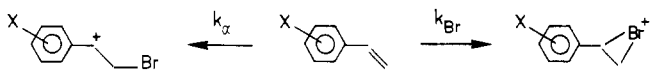
[a] X and Y at C_α and C_β, respectively. Data from ref 30. [b] k in liters per mole per second at 25 °C; experimental and, in parentheses, calculated ($k_{calcd} = k_\alpha + k_\beta + k_{Br}$) data. [c] The sign + means that the corresponding pathway is significant. [d] Experimentally measured (% (−C_α-OMe/(−C_α-OMe + C_β-OMe)) and, in parentheses, calculated (% k_α/k).

tion. In contrast, additivity is observed when the two substituents are both electron-attracting.[30c] These re-



sults can be interpreted in terms of the three-pathway mechanism: electron-donor substituents favor the carbocationic intermediates and electron attractors the bromonium ions. The ρ values (Table I), obtained by the mathematical procedure and limiting situations, are then used to calculate the preferred pathways depending on the substituents. These predictions have been checked by a rate–regiochemistry correlation (Table II). The regioselectivity observed for the methoxy bromide formation agrees with the C_α and (C_β + Br) pathways, as calculated from the rates. However, since three pathways compete, there is a large uncertainty on the relative contributions of each intermediate.

In contrast, in *styrene bromination* only the C_α and Br paths are involved; more quantitative results are obtained. Stereochemical data on the β-methylstyrene reaction indicate bromine bridging dependent on the



ring substituent,[7] but there is no obvious curvature in the $\rho\sigma$ plot of the kinetic data.[8,9] The interpretation of the reactivity–structure relationship in terms of the two competing mechanisms was based[35] on the dependence of the α- and β-methyl effects of the X substituent, the trend of which differs markedly from that observed in hydration, an electrophilic addition unequivocally going through carbocations. Statistically and chemically significant ρ_α and ρ_{Br} values (Table I) have been calculated by the iterative procedure. From these parameters is obtained the relative importance of the carbocation and bromonium pathways (Table III). The stereochemistry implied by these calculations is compared with that of dibromide formation from β-methylstyrenes in methylene chloride. As shown in Table III, there is fair agreement between the two sets of data although kinetic analysis is carried out in methanol and stereochemical analysis in a nonpolar solvent (for solvent effects, see below). In methanol, the methoxy adduct, the major product, is formed 100% stereospecifically and regioselectively, whatever the substit-

(35) Ruasse, M. F.; Argile, A.; Dubois, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 7645.

Table III
***trans*-β-Methylstyrene Bromination in Methanol. The Competition between the Bromonium and Carbocation Pathways. Rate–Stereoselectivity Relationship**

X[a]	log k[b]	% k_B[c]	% trans addn[d]
4-OMe	6.48 (6.54)	0	63 (63)
H	3.51 (3.50)	77	81 (91)
3-CF_3	1.52 (1.58)	93	91 (97)
3,5-$(CF_3)_2$	−0.22 (−0.27)	98	100 (99)

[a] Ring substituent. Data from ref 35. [b] In liters per mole per second at 25 °C. Experimental and, in parentheses, calculated ($k_{calcd} = k_\alpha + k_B$) data. [c] Contribution of the bromonium ion pathway to the overall rate. [d] Trans addition gives the erythro dibromide. Experimental data = % erythro in methylene chloride; in parentheses, calculated data (see ref 35).

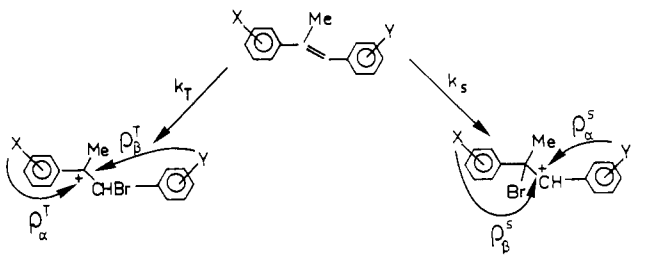
Table IV
α-Methylstilbene Bromination[a] in Methanol. The Competition between the Two Carbocation Pathways. Rate–Regioselectivity Relationship

X[a]	Y[a]	log k[b]	% T[c]
H	H	1.22 (1.22)	100 (100)
H	4-OH	3.21 (3.14)	0 (4)
H	4-OMe	2.15 (2.31)	35 (32)
H	4-Cl	0.81 (0.84)	100 (100)
3-CF_3	4-OMe	1.18 (1.25)	0 (0)

[a] X is the substituent on the ring α to the methylated olefinic carbon atom; Y, on the ring β. Data from ref 36. [b] k in liters per mole per second at 25 °C. Experimental and, in parentheses, calculated ($k = k^T + k^S$) data. [c] Percent T: regiochemistry experimentally measured (% $XC_6H_4C(Me)(OMe)CHBrC_6H_4Y$) and, in parentheses, calculated from kinetics (% (k^T/k)).

uents. Similar results are observed for acetoxy bromides in acetic acid.[12] A plausible interpretation considers the relative rates of conformational equilibration of the carbocation and of the nucleophile attack on more or less dissociated ion pairs.

The *α-methylstilbene series* gives an example of the *competition between the two carbocation pathways*. Two unequivocally different $\rho\sigma$ relationships were ob-



tained for X- or Y-monosubstituted stilbenes.[36] For X substituents, a linear relationship with a high ρ value

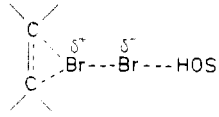
(36) (a) Ruasse, M. F.; Argile, A. *J. Org. Chem.* **1983**, *48*, 202. (b) Argile, A.; Ruasse, M. F. *J. Org. Chem.* **1983**, *48*, 209.

is observed for the complete substituent range. For electron-attracting Y substituents, the $\rho\sigma$ plot is linear with a smaller ρ, whereas electron donors exhibit very large positive deviations. The obvious interpretation is that, for any X and for Y with a positive σ value, only the tertiary pathway is followed; for electron-donating Y, tertiary and secondary carbocations are formed competitively. Investigation of 33 disubstituted α-methylstilbenes, with various sets of substituents favoring one or the other of the two intermediates, gave the ρ values shown in Table I. The regiochemistry of methoxy bromide formation is readily calculated from the kinetic analysis. As shown in Table IV, there is complete agreement between the experimental and calculated values. The exclusive formation of dibromides in methylene chloride and methoxy bromides in methanol is nonstereoselective and substituent-independent. This supports the conclusion that there are no bromonium ion intermediates in the bromination of α-methylstilbenes.

The Solvent Effect on the Multipathway Scheme and the Stereochemistry

Kinetic studies on the competition between the three pathways are feasible only in methanol. The question is, therefore, whether the previous quantitative results can be transposed to other solvents.

Kinetic solvent effects on 1-pentene and on several olefins (Table I) are large and almost independent of the olefin structure.[13a,19,22c] These results, taken with those described above, are consistent with a high polar effect and strong electrophilic assistance but little or no nucleophilic involvement of the solvent in the rate-determining step. The bromination transition states are, therefore, strongly electrophilically but weakly nucleophilically assisted. This must mean that the



solvent mainly influences the anionic but not the cationic part of the activated complex. It can be reasonably inferred that the charge distribution, i.e., the relative contribution of the bromonium and carbocation pathways, does not vary significantly with the solvent.[22]

Several stereochemical data agree with this conclusion: (i) the bromination of alkenes going solely through bromonium ions is always 100% stereoselective, whatever the solvent;[11,12] (ii) the reaction of α-methylstilbenes via carbocations is nonstereoselective in methylene chloride for dibromide formation and also in methanol for methoxy bromides.[36] In contrast, the stereochemistry is observed to be solvent-dependent in the styrene[37] and stilbene[34] series where kinetic data indicate competition between bromonium and carbocation intermediates. This could be attributed to solvent dependence of the multipathway scheme. However, the stereochemistry calculated from rates in methanol is that found in the nonpolar methylene chloride (Table III). Moreover, stereochemical results for the trans olefins are virtually independent of the solvent whereas for the cis olefins it is almost reversed on going from a polar to a nonpolar solvent (Table V). These data are better explained by the relative ease of rotation of the carbocation conformers and the lifetime of the intermediate.[22c,35]

Table V
Solvent Effects on the Stereochemistry of Aryl Olefin Bromination. Percentage of Trans Addition for Dibromide Formation

	β-methylstyrenes[a]		stilbenes[b]	
solvent	trans	cis	trans	cis
CH_2Cl_2	90	78	89	77
CS_2			95	81
$MeNO_2$	81	46		
$PhNO_2$			84	30

[a] Data from ref 37. [b] Data from ref 34a.

Concluding Remarks

Intermediate structures and product selectivities are mainly governed by the double-bond substituents. The 2-fold nature of the intermediate can be viewed as a result of the competition between the entering bromine atom and the substituents in stabilizing the positive charge developed during the reaction. When none of the substituents is able to stabilize the charge better than the bromine atom (alkyl groups, strongly electron-attracting groups, for example), the bromination intermediates are bromonium exclusively. The products are, then, formed 100% stereoselectively whatever the solvent and even when crowded substituents inhibit nucleophile attack.[3,38] Regio- and chemoselectivities, determined by the polar and steric requirements of both the substituents and the nucleophiles, are more difficult to interpret.

When very stable carbocations can be formed (from aryl olefins with electron-donating substituents or enol ethers,[39,41] for example), open intermediates predominate. The products are, then, formed highly regio- and chemoselectively but nonstereoselectively.

Competition between bromonium ion and carbocation intermediates occurs with moderately electron-releasing or -attracting groups. In this situation, the multipathway scheme must be considered in its totality. Predictions of the product selectivities could be made from the relative importance of the three pathways. However, it is difficult, from a physical point of view, to understand how two distinct intermediates, rather than a unique ion whose charge would be distributed between the carbon and bromine atoms, coexist. This difficulty raises the question of the real structure of bromonium ions. In this work we have considered that these bromination intermediates are "onium" ions[4] whose charge is borne only by the heteroatom. But it is likely that this is not the case when bromine is a bridging atom, since NMR data[20] show substantially charged carbon atoms. Theoretical calculations should give information about the structure of these bridged ions. At present, only the ion derived from ethylene and

(37) Pannel, K. H.; Mayr, A. J. *J. Chem. Soc., Perkin Trans. 1* **1982**, 2153.

(38) Marshall, D. R.; Reynolds-Warnhoff, P.; Warnhoff, E. W.; Robinson, J. R. *Can. J. Chem.* **1971**, *49*, 885.

(39) Bienvenue-Goetz, E.; Dubois, J. E. *J. Am. Chem. Soc.* **1981**, *103*, 5388.

(40) Ruasse, M. F. *Isr. J. Chem.* **1985**, *26*, 414.

(41) Dubois, J. E.; Ruasse, M. F.; Argile, A. *J. Am. Chem. Soc.* **1984**, *106*, 4840.

(42) Hegarty, A. F.; Lomas, J. S.; Wright, W. V.; Bergmann, E. D.; Dubois, J. E. *J. Org. Chem.* **1972**, *37*, 2222.

bromine has been examined;[21] the symmetrical cyclic structure is favored by at least 15 kcal mol^{-1} over the open structure. Semiempirical and ab initio calculations aimed at elucidating how substituents can distort the symmetry of the ethylenebromonium ion are in hand.

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