From consideration of the log $(k_{rel})_o$, eq 14 is obtained.

$$\log (k_{rel})_o = (-2.3RT)^{-1}\{[\delta(G^{XD/B})_o - \delta(G^{XC/B})_o] +$$
$$[\delta(G^{XD/s})_o - \delta(G^{XC/s})_o]\} \quad (14)$$

On the right side of eq 14 the first term has the same nature as the one in eq 10 and corresponds to what is called the ordinary electronic effect at the ortho position. The second term represents the proximity electronic effect that we factor as a sum of a through-the-solvent field interaction and a steric interaction, according to eq 15. Making

$$(G^{XD/s})_o = -2.3RT(\lambda^B f_o{}^X f^D + \delta^B e_o{}^X e^D) \quad (15)$$

the necessary substitutions and cancelations, one obtains eq 16, which justifies theoretically the separation of effects

$$\log (k_{rel})_{o,p} = \rho^B(\sigma^D - \sigma^C)(\sigma^X - \sigma^H)_{o,p} +$$
$$\lambda^B(f^D - f^C)(f^X - f^H)_o + \delta^B(e^D - e^C)(e^X - e^H)_o \quad (16)$$

indicated in eq 2, i.e., the legitimacy of the Fujita–Nishioka separation of effects. Considering eq 10 and 14, we may properly mix the log k_{rel} data from reactions A_1 and A_2 in a single correlation (eq 4) if we assume that the ortho and para interactions between X and the reaction site through the nucleus B represent the same kind of phenomenon (ordinary electronic effect). This assumption would be quite reasonable if the two extra nitro groups were absent, but it is still reasonable because the presence of the two nitro groups in the given positions should modify the electronic structure of the nucleus in very similar ways.

Rates of Bromination of Dimethyl Fumarate and of Dimethyl Acetylenedicarboxylate[1]

Susan A. Wolf,[2] Soma Ganguly,[2] and Ernst Berliner*

Department of Chemistry, Bryn Mawr College, Bryn Mawr, Pennsylvania 19010

Rates of bromination of dimethyl fumarate and of dimethyl acetylenedicarboxylate were determined in 50% aqueous acetic acid in the presence of varying amounts of sodium bromide. In the presence of bromide ions both substrates are believed to react by the termolecular Ad_E3 mechanism, and the acetylenic substrate reacts faster than the olefin. The acetylene also reacts faster in the reaction which involves a bimolecular attack by bromine (Ad_E2). Usually olefins react considerably faster than acetylenes in halogenation, and possible reasons for the reversal of the relative rates observed here are discussed.

The problem of the relative reactivities of alkenes and alkynes in various electrophilic addition reactions (k_0/k_a) has been well recognized in recent years and has been critically documented and discussed in a recent review article.[3,4] Briefly, while bond energy data[5] and the greater electron density in alkynes than alkenes would suggest a greater reactivity for alkynes, the experimental data do not usually bear this out. There are those reactions, typified by acid-catalyzed hydration, where double and triple bonds are about equally reactive, and those like halogenation, where simple olefins react many thousand times faster than acetylenes. These large differences in bromination and chlorination have usually been ascribed to the difference in energy of the cationic intermediates involved.[3,4,6]

What has been less often discussed is the puzzling effect of substituents on the relative rates of halogenation of double and triple bonds. *trans*-3-Hexene reacts 3.4×10^5 times faster than 3-hexyne in bromination in acetic acid.[7] An electron-attracting phenyl group reduces the ratio:

trans-1-phenylpropene reacts 5000 times faster than phenylmethylacetylene and styrene 2600 times faster than phenylacetylene. A second phenyl group in the pair stilbene/tolan reduces k_0/k_a to about 250.[8] Introduction of the stronger electron-attracting carbomethoxy group reduces the ratio further, and methyl *trans*-cinnamate is only 27 times more reactive than methyl phenyl-propiolate.[9,10] We have now extended the comparison to the pair dimethyl fumarate and dimethyl acetylenedicarboxylate.

Results and Discussion

The two esters were brominated under identical conditions in 50% aqueous acetic acid (by volume) in the presence of varying amounts of sodium bromide, as was done previously.[9] Under these conditions the rate expression is $-d(Br_2)_T/dt = k_{obsd}(Br_2)_T(A)$, where $(Br_2)_T$ refers to the total titratable bromine and A to the unsaturated substrate. In the presence of bromide ion, the total rate of bromination can then be expressed by eq 1.[9,11] In this

$$-d(Br_2)_T/dt = k_2(Br_2)(A) + k_3(Br_2)(Br^-)(A) \quad (1)$$

equation the first term represents a bimolecular reaction of free bromine with the substrate, and the second term a termolecular, bromide ion assisted process. This term,

(1) Kinetics of Halogenation of Olefins and Acetylenes. 7. For part 6 in this series, see ref 9c.

(2) Taken in part from the Senior Honors Theses of S. A. Wolf and S. Ganguly, Bryn Mawr College, May 1980 and 1984.

(3) Melloni, G.; Modena, G.; Tonellato, U. *Acc. Chem. Res.* **1981**, *14*, 227.

(4) See also: (a) de la Mare, P. B. D.; Bolton, R. In "Electrophilic Additions to Unsaturated Systems", 2nd ed.; Elsevier: Amsterdam, 1982, Chapter 9. (b) Schmid, G. H. In "The Chemistry of the Carbon–Carbon Triple Bond"; Patai, S., Ed.; Wiley: New York, 1978; Part 1, Chapter 8.

(5) Richey, H. G.; Richey J. M. In "Carbonium Ions"; Olah, G. A., Schleyer, P. v. R., Eds; Wiley-Interscience: New York, 1970; Vol. 2, Chapter 21.

(6) Stang, P. J. *Prog. Phys. Org. Chem.* **1973**, *10*, 205. Stang, P. J., Rappoport, Z., Hanak, M., Subramanian, L. R. "Vinyl Cations"; Academic Press: New York, 1979.

(7) (a) Yates, K.; Schmid, G. H.; Regulski, T. W.; Garratt, D. G.; Leung, H. W.; McDonald, R. *J. Am. Chem. Soc.* **1973**, *95*, 160. (b) Modena, G.; Rivetti, F.; Tonellato, U. *J. Org. Chem.* **1978**, *43*, 1521.

(8) Robertson, P. W.; Dasent, W. E.; Milbourne, R. M.; Oliver, W. H. *J. Chem. Soc.* **1950**, 1628.

(9) (a) DeYoung, S.; Ehrlich, S.; Berliner, E. *J. Am. Chem. Soc.* **1977** *99*, 290. (b) Ehrlich S.; Berliner, E. *Ibid.* **1978**, *100*, 1525. (c) DeYoung, S.; Berliner, E. *J. Org. Chem.* **1979**, *44*, 1088.

(10) A ratio of 3 has been reported for the corresponding *acids* in bromination in acetic acid and of 2.5 in methanol. (a) Robertson, P. W. *Rev. Pure Appl. Chem.* **1957**, *7*, 155. (b) Schmid, G. H.; Modro, A.; Yates, K. *J. Org. Chem.* **1977**, *42*, 2021.

(11) Pincock, J. A.; Yates, K. *J. Am. Chem. Soc.* **1968**, *90*, 5643; *Can. J. Chem.* **1970**, *48*, 3332.

however, is kinetically ambiguous and is the kinetic equivalent of k_{Br_3}-$(Br_3^-)(A)$. Because of the tribromide ion equilibrium, k_3K is equivalent to k_{Br_3}-, where K is the dissociation constant of the tribromide ion. Both of these possibilities will have to be considered for this term.

The constants in eq 1 can be evaluated from appropriate plots.[9] The constants k_3 were obtained from the slopes. The constant k_2 is usually obtained as the intercept. But these constants are very small and very close to the origin, and rather than rely on an extrapolation from a limited number of points, k_2 was obtained directly by conducting these runs in the absence of sodium bromide. The bimolecular rate constants, k_2, were thus found to be (7.84 ± 0.46) × 10^{-6} for dimethyl fumarate and (1.80 ± 0.01) × 10^{-4} for dimethyl acetylenedicarboxylate. The termolecular rate constants, k_3, in the same order, are (6.72 ± 0.03) × 10^{-3} and (4.35 ± 0.08) × 10^{-2}. The constants k_{Br_3}- are (1.10 ± 0.01) × 10^{-4} and (7.13 ± 0.14) × 10^{-4}.[12] In all comparable cases the acetylenic ester reacts faster than the olefinic counterpart. The same reversal for this pair of compounds has been observed under different conditions. Diethyl acetylenedicarboxylate has been reported to react 60 times faster than diethyl fumarate in chlorination in acetic acid,[8] and 1.7 times faster in bromination in water.[7a] None of the above ratios are very large, compared with the data cited earlier, and it is perhaps more appropriate to speak of an equalization of rates, rather than a reversal, but it is clear that the large k_0/k_a ratio observed for simple alkenes/alkynes has been eliminated.

The effect of substituents on the k_0/k_a ratio was first recognized and discussed by Robertson and his co-workers.[8] He noted that electron-releasing substituents increase the ratio and electron-attracting ones decrease it and postulated that the halogenation of olefins is affected by substituents to a greater extent than that of acetylenes. This would account for all observed ratios. Put differently, the reactivity ratio of related pairs of compounds increases with their rates. Since that time, others have noted that, in the addition of halogens, olefins are more susceptible to structural effects than acetylenes.[7a,13] Various other observations have been reported in support of the view that electronic effects are transmitted more readily through double than triple bonds.[14]

However, the opposite view has also been expressed,[7b,15] namely, that *larger* substituent effects are observed in alkynes (mainly reported for hydration), and various other explanations have been advanced to account for the k_0/k_a ratios.[3,5,7,16-18] The reasons for the varying reactivity ratios may therefore be quite complex, and there may be several causes, possibly balancing each other, but Robertson's original statement uniquely accounts for the observed facts in halogenation, whatever the reasons might be.

If one wants to compare relative reactivities in halogenation, one must separate the two terms in eq 1.[9a] The first terms are comparable because they represent unambiguously an attack by molecular bromine on the substrate. But two mechanistic possibilities exist for the second term,

and this will be discussed first.

Third-Order Term. The bromide ion assisted bromination of alkynes is now well recognized to represent a termolecular, although not necessarily simultaneous, attack of bromine and bromide ion to the ends of the triple bond with a transition state resembling 1.[11] Similar

1
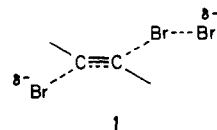
mechanisms have been established for iodination[19] and hydrochlorination,[20] and they are based not only on the kinetics but also on the exclusive anti addition and absence of solvent incorporation. Such a mechanism was, in fact, explicitly proposed for the bromination of dimethyl acetylenedicarboxylate, where complete anti addition in the presence of an excess of lithium bromide in acetic acid was observed.[21] One can therefore assume that the second term in eq 1 is best represented by the Ad_E3 process for the alkyne.

The second term in eq 1 in the bromination of *olefins* has usually been ascribed to the tribromide ion.[22] However, a mechanism similar to 1 has also been proposed.[23] The argument about the meaning of this term has been repeatedly discussed and will not be repeated here,[24] but Bell and co-workers showed that the termolecular mechanism did not agree with the expected product composition for most substrates, except in the single case of the bromination of diethyl fumarate.[25] The bromination of dimethyl fumarate may then be considered to represent an authentic case of an Ad_E3 process. Other examples of this mechanism in olefinic hydrohalogenation[26] and bromination[27] have since been reported.

The literature is replete with reports that fumaric acid undergoes addition of bromine anti, both in the absence[28] and presence[23a] of bromide ions. Also, the rate of bromination of fumaric acid and its ester is extremely slow.[29,30] In the present case, k_{Br_3}- is 14 times larger than k_2, which would imply that Br_3^- is a better electrophilic brominating agent than Br_2.[31] If, however, both the acetylenic and the olefinic substrates are accepted to react by the same Ad_E3 mechanisms, their rates of bromination can be compared directly and the acetylene reacts 6.5 times faster than the olefin.[32] The reversal in rates can then be accounted for

(12) The rate constants k_2 and k_{Br_3}- are in M^{-1} s^{-1} and k_3 is in M^{-2} s^{-1}.

(13) Schmid, G. H.; Modro, A.; Yates, K. *J. Org. Chem.* **1980**, *45*, 665. Gelin, R.; Pigasse, D. *Bull. Soc. Chim. Fr.* **1971**, 2186.

(14) Grindley, T. B.; Johnson, K. F.; Katritzky, A. R.; Keogh, H. J.; Thirkettle, C.; Topsom, R. D. *J. Chem. Soc., Perkin Trans. 2* **1974**, 282 and references therein.

(15) Allen, A. D.; Chiang, Y.; Kresge, A. J.; Tidwell, T. T. *J. Org. Chem.* **1982**, *47*, 775. Kornprobst, J. M.; Dubois, J. E. *Tetrahedron Lett.* **1974**, 2203.

(16) Pincock, J. A.; Yates, K. *Can. J. Chem.* **1970**, *48*, 2944.

(17) Modena, G.; Tonellato, U. *Adv. Phys. Org. Chem.* **1971**, *9*, 185.

(18) (a) Reference 10b. (b) Ruasse, M. F.; Dubois, J. E. *J. Org. Chem.* **1977**, *42*, 2689.

(19) (a) Wilson, M. H.; Berliner, E. *J. Am. Chem. Soc.* **1971**, *93*, 208. (b) Mauger, E.; Berliner, E. *Ibid.* **1972**, *94*, 194. (c) Cunningham, V. L.; Berliner, E. *J. Org. Chem.* **1974**, *39*, 3731.

(20) Fahey, R. C.; Lee, D. J. *J. Am. Chem. Soc.* **1968**, *90*, 2124, **1966**, *88*, 5555.

(21) Shilov, E. A.; Smirnov-Zamkov, I. V. *Izv. Akad. Nauk. SSSR, Otdel. Khim. Nauk.* **1951**, 32.

(22) Bartlett, P. B.; Tarbell, D. S. *J. Am. Chem. Soc.* **1936**, *58*, 466.

(23) (a) Nozaki, K.; Ogg, R. A., Jr. *J. Am. Chem. Soc.* **1942**, *64*, 697. Kanyaev, N. P. *Zh. Obshch. Khim.* **1959**, *29*, 841.

(24) For references see ref 9a and 9c.

(25) Atkinson, J. R.; Bell, R. P. *J. Chem. Soc.* **1963**, 3260. Bell, R. P.; Pring, M. *J. Chem. Soc. B.* **1966**, 1119.

(26) Fahey, R. C.; McPherson, C. A. *J. Am. Chem. Soc.* **1971**, *93*, 2445. Fahey, R. C.; McPherson, C. A.; Smith, R. A. *Ibid.* **1974**, *96*, 4534.

(27) de la Mare, P. B. D.; Wilson, R. D. *J. Chem. Soc., Perkin Trans. 2* **1977**, 2048, 2055, 2062.

(28) Fittig, R.; Petri, C. *Liebigs Ann. Chem.* **1879**, *195*, 56. McKenzie, A. *J. Chem. Soc.* **1912**, *101*, 1196. Frankland, P. F. *Ibid.* **1912**, *101* 654. See also: ref 23a.

(29) Hansen, N. W.; Williams, D. M. *J. Chem. Soc.* **1930**, 1059. See also: ref 23a.

(30) Rhinesmith, H. S. "Organic Syntheses"; Wiley: New York, 1948; Collect. Vol. 2, p 177.

(31) For similar observations, see ref 23b, 25, and 38.

(32) In 75% aqueous methanol the ratio of the k_3 terms is about 18. Taken from the Senior Honors Theses of E. Moser and J. J. Littzi, Bryn Mawr College, May 1981 and 1983.

if it is assumed that although the reactions are termolecular, the extent of bond formation to the nucleophile and electrophile need not have progressed to the same extent in the transition state. In the presence of the strongly electron-attracting carbomethoxy groups the bonding of the nucleophile will have progressed further than bonding to the electrophile,[19b,c] resulting in what is more like a nucleophilic attack. The fast reversible formation of a charge-transfer complex followed by a nucleophilic attack by bromide ion is another possibility, although it is not required by the kinetics. The greater propensity of triple bonds than double bonds toward nucleophilic attack is well documented.[33] It is not likely, however, that the data cited in the introduction can be accounted for by an increasing nucleophilic participation in the rate-determining step as the electron-attracting power of the substituents increases, because these ratios are based on a comparison of the k_2 terms, in which external bromide ion is not involved.

Second-Order Term. Dimethyl acetylenedicarboxylate reacts about 20 times faster than dimethyl fumarate with molecular bromine. It is possible to ascribe this reversal also to a nucleophilic attack. Nucleophilic bromination by bromine has been postulated particularly for the acid-catalyzed halogenation of α,β-unsaturated carbonyl compounds.[34] Although such an involvement cannot be categorically ruled out, it is not likely to play a role here. It is not clear how fast or slow such a reaction should be, but in authentic cases of nucleophilic additions alkynes react many times faster than alkenes.[33,35] On the other hand, the very low reactivity of the two esters in the k_2 process is more easily accounted for by a very slow electrophilic attack, as is also the fact that the anion of fumaric acid reacts faster than the acid.[36] The exclusive anti addition to fumaric acid has, of course, provided the textbook case for the bromonium ion intermediate.[37] This was not only required for stereochemical reasons but is also very reasonable on electronic grounds, because a positive charge next to a highly electron-withdrawing ester group cannot be easily dispersed and bromine participation via the bridged ion is therefore much more likely here, as well as in the acetylene.[38] The bromination of dimethyl acetylenedicarboxylate in acetic acid and in the absence of bromide ions has been reported to produce about equal amounts of cis and trans products, and this has been ascribed to a free radical chain process, both in the presence of and absence of light.[21] Our kinetic data in the more polar aqueous acetic acid do not support the occurrence of a chain reaction. Furthermore, in water in the complete absence of light, the acid affords almost exclusively the anti adduct, with only very small amounts of the cis isomer and no solvent-incorporated products.[39] This reaction therefore probably also proceeds through a fully bridged or a strongly partially bridged ion rather than an open one. If both reactions were to proceed through open ions, the situation might be similar to hydration, where k_0/k_a is strongly diminished. But if both reactions involve bridged ions, or the olefin a bridged and the alkyne a partially bridged ion, the greater reactivity of the acetylene is not easily explained. The many, often quite ingenious, explanations of the different reactivity ratios have been advanced to account for *high* k_0/k_a ratios, not for *low* ones. But the recently calculated molecular polarizabilities, which agree well with experimental data, show that olefins are more polarizable than acetylenes.[40] It is tempting to suggest, in agreement with Robertson's ideas, that the powerfully electron-withdrawing ester groups deplete the electron density in the olefin more than in the acetylene. This may then be a case where the subtle balance of factors on which k_0/k_a depends[4a] may have been sufficiently tilted to favor the acetylene and to equalize the rates.

Experimental Section

Kinetic Determinations. These were carried out as described before at 25.00 ± 0.05 °C.[9] Runs were conducted at seven different concentrations of NaBr for dimethyl fumarate (0.020–0.50 M) and at six concentrations for dimethyl acetylenedicarboxylate (0.050–0.50 M) not counting the runs in the absence of bromide ion. In the previous studies runs were conducted at a constant ionic strength (NaClO$_4$), but this was abandoned here because it was found that unlike in the earlier investigations the rates decreased with an increase of NaClO$_4$. Test runs at two different concentrations of NaBr and NaClO$_4$ showed that this does not affect the reversal in k_0/k_a.

Runs were carried out at least in duplicate, and rate constants were calculated with a least-squares program. Except in a very few cases, the probable error in individual rate constants was usually less than 1% and it averaged 1.5% for all runs. Rate constants of duplicate and triplicate runs usually agreed within less than 1%. In dimethyl fumarate runs at the two lowest NaBr concentrations (0.020 and 0.050 M) the agreement was less precise and the constants differed from the mean by 13.9% and 5.4%, respectively. The deviations from the mean in all duplicate and triplicate runs averaged 2.1%. In the two runs above, the initial bromine concentration was about 0.002 M, but in all others it was about 0.008 M and the unsaturated substrate was present in a five- to tenfold excess, depending on the reactivity of the substrate. All runs were usually carried to at least 50% completion. The errors quoted for k_3 and $k_{Br_3^-}$ are probable errors obtained from the least-squares plots. Errors in k_2 are deviations from the mean of duplicate runs. A value of 0.0164 M was used for K.[42]

(33) Dickstein, J. I.; Miller, S. I. In "The Chemistry of the Carbon–Carbon Triple Bond"; Patai, S., Ed.; Wiley: New York, 1978; Part 2, Chapter 19.

(34) de la Mare, P. B. D.; Roberston, P. W. *J. Chem. Soc.* **1945**, 888. Rothbaum, H. P.; Ting, I.; Robertson, P. W. *Ibid.* **1948**, 980. See also: ref 4a, Chapter 11.

(35) See, for instance: Evans, C. M.; Kirby, A. J. *J. Chem. Soc., Perkin Trans. 2* **1984**, 1269, who report a rate factor of 10⁴.

(36) Terry, E. M.; Eichelberger, L. *J. Am. Chem. Soc.* **1925**, *47*, 1067.

(37) Roberts, I.; Kimball, G. E. *J. Am. Chem. Soc.* **1937**, *59*, 947. In addition to the bromonium ion mechanism, a mechanism involving 1,4-addition of molecular bromine to the dianions of maleic and fumaric acids has been proposed, see: Weiss, H. *J. Am. Chem. Soc.* **1977**, *99*, 1670.

(38) For a similar reason bromine participation has been suggested for the bromination of highly deactivated styrenes, see: Rolston, J. H.; Yates, K. *J. Am. Chem. Soc.* **1969**, *91*, 1483.

(39) Ott, E. *Liebigs Ann. Chem.* **1912**, *392*, 245. See also: Ott, E.; Packendorff, K. *Chem. Ber.* **1931**, *64*, 1324. In the early literature (see: Michael, A. *J. Prakt. Chem.* **1892**, *46*, 209. Lossen, W. *Liebigs Ann. Chem.* **1906**, *348*, 261) there are reports that between 70% and 88% of trans products are formed in the bromination of the acid or the ester, the remainder being the cis adducts; but these reactions were often carried out in light in order to speed them up. Ott discussed these early reports in detail. He also remarked that dibromofumaric acid (and its ester) is actually the labile form and is converted by heat, or by bromine in light, to the more stable dibromomaleic acid, which he therefore considered a secondary reaction product. He reported that by his procedure the amount of dibromomaleic acid was too small to be isolated.

(40) Miller, K. J.; Savchick, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 7206.

(41) Sugden, S.; Whittaker, H. *J. Chem. Soc.* **1925**, *127*, 1868.

(42) Berliner, E.; Beckett, M. C. *J. Am. Chem. Soc.* **1957**, *79*, 1425.