Bromination of *trans*-Cinnamic Acid and Its Methyl Ester[1]

Susan DeYoung[2] and Ernst Berliner*

Contribution from the Department of Chemistry, Bryn Mawr College, Bryn Mawr, Pennsylvania 19010

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The kinetics of the bromination of *trans*-cinnamic acid, its sodium salt, and methyl ester were studied in 75% aqueous acetic acid in the presence of varying amounts of sodium bromide, sodium acetate, and sodium perchlorate. The results of the study are compared with the results of a recent study on the bromination of the acetylenic counterpart, phenylpropiolic acid. The reaction of cinnamic acid and its derivatives follows the two-term rate equation $-d(Br_2)_T/dt = k_2(Br_2)(olefin) + k_3(Br_2)(Br^-)(olefin)$. Only two products were isolated under all conditions, *erythro*-2,3-dibromo-3-phenylpropanoic acid and *erythro*-2-bromo-3-hydroxy-3-phenylpropanoic acid, or their esters, which are formed as a result of complete stereospecific and regiospecific anti addition. The first term in the rate equation involves a bimolecular attack (Ad_E2) of bromine on the substrate and a weakly bridged bromonium ion intermediate with some charge on the benzylic carbon atom. The third-order term is suggested to proceed through a bimolecular electrophilic attack by the tribromide ion, but a termolecular, not necessarily synchronous, attack by bromine and bromide ion (Ad_E3) cannot be completely ruled out.

The kinetics and products of the bromination of phenylpropiolic acid, its sodium salt, and ethyl ester have recently been reported.[3] As a companion piece to this study, we now report the bromination of *trans*-cinnamic acid, sodium cinnamate, and methyl cinnamate, as well as the products of the reaction, in 75% aqueous acetic acid. The emphasis is on the similarities and differences in mechanistic detail between olefinic and acetylenic halogenations.

There is extensive literature on the bromination of *trans*-cinnamic acid, both with regard to the products of the reaction as well as its kinetics in a variety of polar and nonpolar solvents.[2] For purposes of comparison, it was necessary, however, to carry out the reactions under exactly the same conditions as the reaction of its acetylenic counterpart.

Results

The kinetic characteristics of the bromination of *trans*-cinnamic acid and its derivatives are very similar to those of the reaction of phenylpropiolic acid. They can therefore be summarized only briefly, with reference to the earlier study, where some of the arguments are presented in greater detail.[3] They are as follows. (1) The observed rate law is $-d(Br_2)_T/dt = k_{obsd}(Br_2)_T(olefin)$, where $(Br_2)_T$ is the total titratable bromine concentration. The reaction is strictly of the second order, and a change of the acid and bromine concentrations by factors of 3 does not change k_{obsd}. The term which is of higher order in bromine, first observed by Robertson in the bromination of cinnamic acid,[4] is thus eliminated under the present conditions. (2) The dependence of the rate on the bromide ion concentration (Table I) at a constant ionic strength, maintained with sodium perchlorate, indicates that the reaction follows the two-term rate equation 1. This is true for the acid ($k_2 = (2.86 \pm 0.08) \times 10^{-1}$, $k_3 = 1.93 \pm 0.03$), the sodium salt ($k_2 = (3.04 \pm 0.03) \times 10^{-1}$, $k_3 = 2.01 \pm 0.01$), and the methyl ester ($k_2 = (1.30 \pm 0.04) \times 10^{-1}$, $k_3 = 1.90 \pm 0.01$).[5] The rate constant k_3 refers to the termolecular bromide ion assisted reaction and is used here without prejudice to the actual brominating entity involved (see later) because it is obtained directly from the appropriate kinetic plots[3] (Figure 1). By contrast, the reaction of phenylpropiolic acid and its salt did not have a k_3 term, although that of its ester does. (3) The rate of reaction of the acid increases linearly with sodium perchlorate concentration (0.10–0.40 M) at a constant bromide ion concentration. (4) Sodium acetate increases the rate of reaction of the acid (the catalytic constant k_{OAc^-} is $(4.00 \pm 0.04) \times 10^{-1}$ M^{-1} s^{-1}) at constant NaBr and μ, and of sodium cinnamate ($k_{OAc^-} = (3.25 \pm 0.01) \times 10^{-1}$ M^{-1} s^{-1}) (Table I). The free acid and its sodium salt react at similar rates, and the rates are similarly influenced by sodium acetate. As discussed before,[3] this is taken to indicate that the actual substrate that is brominated is the anion of the acid. This view is supported by the observation that the bromination rate of the ester is not affected by sodium acetate (Table I). Furthermore, perchloric acid at first decreases the rate of reaction of the acid, but then slightly increases it, probably as the ionic strength effect of perchlorate ion overbalances the rate-decreasing effect caused by protonation of the anion. (5) The activation energy, E_a, for reaction of the acid, obtained from an Arrhenius plot taken from rate constants at six different temperatures from 20.0–45.0 °C (NaBr = 0.10 M), is 12.1 ± 0.2 kcal/mol, and the activation entropy at 25 °C is −26.6 ± 0.1 eu. (6) The products of the reaction of the acid and the ester are shown in Table II. Isolation runs were conducted under three different conditions, paralleling the kinetic runs, in the absence of bromide ion, and in the presence of low (0.10 M) and high (0.50 M) concentrations of sodium bromide. Runs of the ester were also conducted in the presence of sodium acetate (0.10 and 0.40 M). Only two products were formed under all conditions, *erythro*-2,3-dibromo-3-phenylpropanoic acid and *erythro*-2-bromo-3-hydroxy-3-phenylpropanoic acid (or their esters). The products were identified by comparison of GLC retention times and mass spectral data with authentic samples. No neutral decarboxylation products were found. (7) An increase of water in the reaction mixture to 50% aqueous acetic acid increases the rate of reaction of the acid considerably ($k_2 = 2.25 \pm 0.03$, $k_3 = 8.87 \pm 0.20$).[5]

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

The relative reactivity (k_2) of the olefinic and acetylenic substrates, obtained under identical conditions, has been discussed in an earlier communication.[6]

Discussion

Second-Order Term. The kinetic term which corresponds to the expression $k_2(Br_2)(olefin)$ involves an electrophilic attack of free bromine on the olefinic substrates, both for the acid and the ester. This attack may be preceded by a charge-transfer complex between the olefin and bromine, as often suggested,[7] but the kinetics do not require it. The attack is an electrophilic one because the anion of the acid reacts faster than the acid and ester. The nature of the intermediate is suggested by the products of the reaction. The only products isolated were those formed by anti addition, both the dibromide and the bromohydrin. They are formed in about equal proportions in the absence of external bromide ion, but the amount of dibromide increases with external bromide ion, as observed with other substrates,[8b] until it becomes the exclusive product at a NaBr concentration of 0.50 M. No other

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Table I. Bromination of *trans*-Cinnamic Acid and Its Derivatives[a]

NaBr, M	$NaClO_4$, M	NaOAc, M	$HClO_4$, M	$k_{obsd} \times 10^2$, M^{-1} s^{-1} *trans*-cinnamic acid[b]	*trans*-sodium cinnamate[c]	methyl *trans*-cinnamate[d]
0.10	0.40			4.67	5.12	3.16
0.20	0.30			3.40	3.72	2.66
0.30	0.20			3.16	3.22	2.50
0.40	0.10			2.82	2.96	2.40
0.45	0.05				2.87	2.34
0.50				2.67		
0.10	0.10			3.82		
0.10	0.20			4.08		
0.10	0.30			4.38		
0.10	0.40			4.56		
0.20	0.26	0.04		5.00	5.00	
0.20	0.22	0.08		6.60	6.32	
0.20	0.20	0.10		7.45	6.95	
0.20	0.18	0.12		8.18	7.60	
0.10	0.30		0.10	3.76		
0.10	0.20		0.20	3.34		
0.10	0.10		0.30	3.40		
0.45	0.05					2.34
0.45	0.04	0.01				2.35
0.45	0.02	0.03				2.35

[a] The concentration of the olefinic substrates was $\sim 4 \times 10^{-3}$ M and that of bromine $\sim 1 \times 10^{-3}$ M. [b] Registry no., 140-10-3. [c] Registry no., 18509-03-0. [d] Registry no., 1754-62-7.

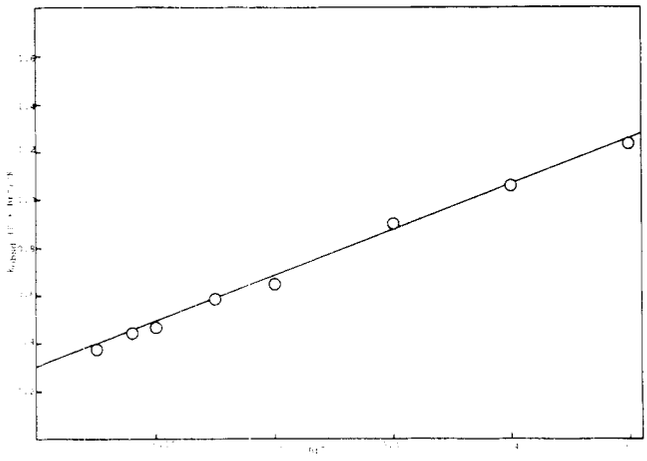


Figure 1. The dependence of the rate of bromination of *trans*-cinnamic acid on the bromide ion concentration.

Table II. Product Distribution

substrate	NaBr, M	NaOAc, M	% dibromide[a]	% bromohydrin[b]
trans-cinnamic acid			48.6	51.4
trans-cinnamic acid	0.10		68.0	32.0
trans-cinnamic acid	0.50		100.0	
methyl *trans*-cinnamate			52.5	47.5
methyl *trans*-cinnamate	0.10		65.2	34.8
methyl *trans*-cinnamate	0.50		100.0	
methyl *trans*-cinnamate	0.40	0.10	62.0	38.0
methyl *trans*-cinnamate	0.10	0.40	56.3	43.7

[a] *erythro*-2,3-Dibromo-3-phenylpropanoic acid or its methyl ester. [b] *erythro*-2-Bromo-3-hydroxy-3-phenylpropanoic acid or its methyl ester.

products were found, and 1% of the *threo*-dibromide or of the *erythro*-bromohydrin could have been detected in an excess of the *erythro*-dibromo acid. Acetate ion increases the amount of bromohydrin, but not by very much.[9] Any bromo acetate that may have been formed initially is assumed to have been hydrolyzed to the bromohydrin on workup. By contrast, in the bromination of ethyl phenylpropiolate, 100% trans addition was achieved already at a lower concentration of NaBr (0.1 M) and acetate had no effect in the presence of bromide ion.[3] The present product distribution argues strongly for a cationic intermediate which is captured by bromide ion, acetate ion, and/or the solvent.

The complete stereospecificity in this reaction rules out an open carbonium ion intermediate. Open carbonium ions have frequently been postulated when they are next to a phenyl group, and they invariably result in a mixture of cis and trans products. In the present case the carboxyl or carboethoxyl groups will tend to destabilize the carbonium ion. On the other hand, these groups may in themselves be configuration-holding groups[10] and the carboxylate ion in particular is a better bridging group than bromine.[11] It does not, however, seem likely that such bridging is involved here because the product distribution is almost the same for the acid and the ester, and the anion must be expected to be a much better bridging group than the ester group. Besides, such bridging ought to lead to the opposite stereochemistry.

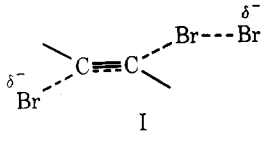
While a completely open carbonium ion can be ruled out, of the remaining two possibilities, a fully bridged bromonium ion and an incompletely or weakly bridged one, the latter is preferred. It is not clear if a stable bromonium ion should lead to solvent-incorporated products because in the best documented cases of such ions, in the bromination of alkenes in acetic acid, the amount of solvent incorporation is very small,[12] while it is considerable here. Also, a symmetrically bridged ion might be expected to lead to some anti-Markownikoff products, whereas the addition here is not only completely stereospecific but also regiospecific; none of the nonregiospecific 3-bromo-3-phenyl-2-hydroxypropanoic acid could be detected in the reaction mixtures, which is in full agreement with the results of similar recent studies.[13] An unsymmetrically weakly bridged ion with some charge on the benzylic carbon atom best accounts for the products. Weak or unsymmetrical bridging with some carbonium ion character has often been considered,[14] and has been suggested to account for the mixture of cis and trans products formed in the bromination of substituted styrenes.[8a,b,15] The exact extent and nature of bridging in styrenes is still an unsettled question, and the suggestion

has also been made that in the bromination of styrenes the rate-determining transition state may be completely bridged, but a second, product-determining intermediate is not.[16] In any case, some intermediate which allows for lack of stereospecificity must be present in the styrenes, but in cinnamic acid bromination the bridging must be stronger or sufficiently strong to prevent free rotation or to lead to faster trans orientation of bromide ion (in the absence of external Br^-) than collapse to the cis products. It could be argued that such a collapse to cis products, even from an open ion, is conformationally unfavorable because it would lead to eclipsing of two large bromine atoms or, after rotation around the C–C bond, to unfavorable eclipsing of the phenyl and carboxyl groups. But this cannot be the cause for the stereospecific trans addition here because in other solvents, and in the case of substituted cinnamic acids, substantial amounts of the threo adducts are formed.[13] One is thus left with the conclusion that the carboxyl group plays a specific role in this system in encouraging bromine bridging, perhaps for steric, conformational, or electronic reasons, or because its destabilizing effect discourages open carbonium ion formation.

In the bromination of phenylpropiolic acid and ester it was necessary to postulate a free vinylic carbonium ion for the first term in eq 1, even though such ions are considered to be much more difficult to generate than the free carbonium ions expected from cinnamic acid. This may reflect more the difficulty of forming the *bridged* vinylic bromonium ion, with its attending strain, than the difficulty of forming the open ions.

The increase in rate with increase in ionic strength or with an increase of the water content in the solvent is expected for this kind of reaction.

Third-Order Term. While the first term in eq 1 corresponds to a rather similar mechanistic step in olefinic and acetylenic bromination, namely, a bimolecular attack of free bromine on the unsaturated substrates with the formation of a cationic intermediate, the same cannot be stated a priori of the second term in eq 1. In acetylenic bromination this "bromide ion assisted" bromination is now recognized to represent a separate, although not necessarily simultaneous, attack of bromine and bromide ion at the ends of the triple bond[17] with a transition state resembling I, or, less likely, in the fast formation of an acetylene–bromine complex, followed by rate-determining bromide ion attack. This results in complete anti addition and no solvent incorporation. The second term in eq 1 is, however, the kinetic equivalent of eq 2. Here the halogenating agent is the tribromide ion. Because of the tribromide ion equilibrium, the terms k_3K and $k_{Br_3^-}$ are equivalent; K is the dissociation constant of the tribromide ion. The mechanistic meaning of the two second terms in eq 1 and 2 has been the subject of a long standing debate, precisely because kinetics cannot distinguish between them.[18] The tribromide ion was first proposed as a halogenating species for olefins by Bartlett and Tarbell,[19] and their interpretation has been generally accepted for the bromination of olefins. The tribromide ion can be considered a carrier of bromine, though a less powerful electrophile than bromine. The two bimolecular attacks (by Br_2 and Br_3^-) are assumed to occur concurrently and lead to similar cationic intermediates. The tribromide ion has also been recognized as a weak brominating agent in electrophilic aromatic substitution.[20]



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$$-d(Br_2)_T/dt = k_2(Br_2)(\text{olefin}) + k_{Br_3^-}(Br_3^-)(\text{olefin}) \quad (2)$$

On the other hand, the possibility was early considered that the term might represent discrete attacks, not necessarily simultaneous, by bromine and bromide ion,[18] as in eq 1, and as apparently first suggested by Nozaki and Ogg.[21] The most far reaching interpretation was proposed by Kanyaev in 1959,[22] who noted that in the bromination of some strongly deactivated substrates $k_{Br_3^-}$ was greater than k_{Br_2}, which would imply the unlikely proposition that Br_3^- is a better electrophile than Br_2. He therefore proposed that the "tribromide ion" reacts in a fashion similar to that shown in I by separate bromine and bromide ion attack. He suggested that at least for some substrates reaction of "tribromide" leads exclusively to dibromide ion formation and reaction of bromine exclusively to bromohydrins. Bell and Atkinson,[23] in an investigation of a larger number of olefins, concluded that Kanyaev's mechanism did not agree with the product composition predicted by that mechanism, but that for some highly deactivated substrates Kanyaev's suggestion could not be completely ruled out. Their main conclusion, though, was that the Bartlett–Tarbell mechanism must be the correct one. An identical conclusion was reached by Rolston and Yates,[8c] who, however, also noted that in strongly deactivated substrates $k_{Br_3^-} > k_{Br_2}$. Nevertheless, "there is no certain way of distinguishing between the two possibilities",[24] and a termolecular attack continues to be considered for this term. A dual pathway, depending on the reactivity of the substrate, has also been proposed.[22,25] The termolecular mechanism has now been well established by Fahey and co-workers for the addition of HCl and HBr to some olefins,[26] and has most recently been considered for bromination by de la Mare and Wilson.[27]

If in the strict interpretation of Kanyaev the bimolecular attack affords exclusively bromohydrin and the termolecular attack exclusively dibromide, the percent contribution of the two separate processes can be calculated and is shown in Table III for the acid and the ester. The data show that the calculated overall rate constants agree with those found, but the product distribution is greatly at variance with the above hypothesis. The calculated contribution to the total reaction at a 0.1 M bromide ion concentration is 59.6% for reaction by molecular bromine and 40.4% for reaction by bromine–bromide ion. This should reflect the relative amounts of products obtained. The actual amounts are 32.0% of the former and 68.0% of the latter. Similar discrepancies are observed with the ester. At a 0.5 M NaBr concentration the mechanism predicts 77.1 and 86.8% dibromide formation for the acid and the ester, respectively, whereas the observed amounts are 100% dibromide in both cases. Expressed differently, at 0.1 M NaBr the calculated ratio of dibromide/bromohydrin in the case of the acid is 0.68 and of the ester 1.46, whereas the ratios found are 2:13 and 1:87. Nor is the bromohydrin formed by a termolecular attack of bromine and the solvent, as is implied,[22] because the rate of reaction of the ester is independent of sodium acetate concentration.

These calculations argue strongly against a "bromide ion assisted" process and favor the tribromide ion as the attacking species. It is noted, however, that *more* dibromide is formed in all cases than predicted by the termolecular mechanism. If one assumes, as is usually done, that some of the dibromide is formed from the bimolecular attack by Br_2, then it becomes less easy to rule out completely a bromine–bromide attack for the second term. If the strict Kanyaev mechanism can be ruled out, there is no compelling evidence to assume that it contributes at all, but no compelling evidence to rule it out.[28]

Activation parameters have sometimes been adduced in support of the Ad_E3 mechanism because the k_3 term is usually characterized by a large negative activation entropy. It is −45.7 eu in the bromination of ethyl phenylpropiolate.[3] The value of −26.6 eu here observed is closer to the magnitude

Table III. Calculated Contributions of the Two k_2 and k_3 Processes

NaBr, M	$k_2K/(K + [Br^-])$ $\times 10^2$	$k_3K[Br^-]/(K + [Br^-])$ $\times 10^2$	$k_{obsd} \times 10^2$, L mol^{-1} s^{-1}	$k_{calcd} \times 10^2$, L mol^{-1} s^{-1}	% $k_2K/(K + [Br^-])$	% $k_3K[Br^-]/(K + [Br^-])$
		A. Bromination of *trans*-Cinnamic Acid				
0.10	2.83	1.91	4.67	4.74	59.6 (32.0)[a,b]	40.4 (68.0)[a,c]
0.20	1.49	2.01	3.40	3.50	42.6	57.4
0.30	1.01	2.05	3.16	3.06	33.0	67.0
0.40	0.76	2.07	2.82	2.83	27.0	73.0
0.50	0.62	2.08	2.67	2.70	22.9 (0)[a,b]	77.1 (100)[a,c]
		B. Bromination of Methyl *trans*-Cinnamate				
0.10	1.29	1.88	3.16	3.17	40.7 (34.8)[a,b]	59.3 (65.2)[a,c]
0.20	0.68	1.98	2.66	2.66	25.5	74.5
0.30	0.46	2.02	2.50	2.48	18.6	81.4
0.40	0.35	2.03	2.40	2.38	14.6	85.4
0.45	0.31	2.03	2.34	2.34	13.2 (0)[a,b,d]	86.8 (100)[a,c,d]

[a] Figures in parentheses represent the observed product distribution. [b] Bromohydrin. [c] Dibromide. [d] (NaBr) = 0.50 M.

expected for a bimolecular reaction, but our parameters are composite because they were determined at a 0.1 M bromide ion concentration, where the contribution of the third-order term is only 40%. Nevertheless, the activation entropy is not in disagreement with the assumption that both terms correspond to a bimolecular attack.

The values calculated for the bimolecular rate constants for reaction by tribromide ion ($k_{Br_3^-}$) are 2.12×10^{-2} M^{-1} s^{-1} for the acid and 2.09×10^{-2} M^{-1} s^{-1} for the ester. These are smaller than the constants for the bimolecular attack of Br_2(k_{Br_2}), which lends further support to the assumption that the tribromide ion acts as a weak electrophile in this reaction. The values for the ratio $k_{Br_3^-}/k_2$ (0.074 for the acid and 0.16 for the ester) are similar to the ratio found by Bell and Atkinson for the bromination of ethyl cinnamate in water (0.07).[23] All the evidence thus suggests that the second term in the mechanism involves the tribromide ion, yet a contribution from the termolecular mechanism cannot be ruled out. The possibility of such an attack is permissive rather than compelling.

Experimental Section

Materials. The instrumentation, inorganic salts, and glacial acetic acid were as described before.[3]

trans-Cinnamic acid (Aldrich Chemical Co., zone refined 99.9%) was used without further purification. Sodium cinnamate was prepared as described for the acetylenic acid.[3] Methyl cinnamate, twice recrystallized from methanol, had mp 34.8–35.4 °C (lit.[29] 35 °C). The compounds needed for comparison purposes were prepared according to literature procedures. *erythro*-2,3-Dibromo-3-phenylpropanoic acid, after two crystallizations from $CHCl_3$, had mp 201–202 °C (lit.[30] 200–202 °C). *threo*-2,3-Dibromo-3-phenylpropanoic acid, obtained in small yield by bromination of *trans*-cinnamic acid in CS_2, had mp 86.2–87.2 °C (lit.[31] 89–91 °C). After esterification, the product was found by GLC to be a mixture consisting of 27.9% of starting material, 7.8% of the erythro isomer, and 64.3% of the desired threo compound. The mass spectrum corresponding to the peak produced by this isomer had the characteristic peaks at *m/e* 169 and 171 for the bromotropylium ion,[32] as well as other expected peaks. *erythro*-2-Bromo-3-hydroxy-3-phenylpropanoic acid[33] melted at 124.6–125.6 °C after two crystallizations from toluene (lit.[32] 125 °C). The mass spectrum of the ester afforded the characteristic peak at *m/e* 107 for the oxotropylium ion but did not have the peaks at *m/e* 169 and 171 mentioned above.[32] A sample of *threo*-2-bromo-3-hydroxy-3-phenylpropanoic acid of mp 64–65 °C (lit.[32] 65 °C) was kindly provided by Professor de la Mare.[34] The mass spectral data of the threo isomer were identical with those of the erythro isomer. *trans*-α-Bromocinnamic acid, prepared from the *erythro*-dibromo acid, had mp 131–132 °C (lit.[35] 130–131 °C). Methyl *erythro*-2,3-dibromo-3-phenylpropanoate, prepared by bromination of methyl *trans*-cinnamate,[36] had mp 115–116.6 °C after crystallizations from CCl_4 (lit.[35] 117 °C); it contained about 12% of starting material by GLC. The methyl ester of the *threo*-dibromo acid was prepared from the acid with 1-methyl-3-*p*-tolytriazene (Willow Brook Laboratories) and melted at 52–53 °C (lit.[37] 52–53 °C). Methyl *erythro*-2-bromo-3-hydroxy-3-phenylpropanoate, prepared by standard esterification and crystallization from ligroin, had mp 60.4–61.2 °C (lit.[38] 64 °C) and was free of other isomers. The methyl ester of the isomeric *threo*-acid was prepared with the triazene as above.

Product Isolation. All isolation runs were done at 25 °C at least in duplicate with the same concentration of reagents as in the kinetic runs, except that the volumes were 200, 500, or 1000 mL. An aliquot was removed to determine the initial Br_2 concentration. After the reaction was completed (overnight), the solvent was removed with a rotary evaporator attached to a vacuum pump. The residue was analyzed exactly as described before.[3] The esters were analyzed directly, but the acids were first esterified with 1-methyl-3-*p*-tolytriazene. In runs designed to test for neutral decarboxylation products, the acids were extracted with $NaHCO_3$ solution from an ether solution and after workup no neutral fraction was obtained. A second check was made by omitting the solvent evaporation, extracting the product mixture with ligroin, and extracting the acids with $NaHCO_3$. Again, no neutral products were detected.

Products were identified in each case by comparison of retention times with those of authentic samples. Additionally, most runs were checked by use of a second gas chromatograph, connected to the mass spectrometer, and all products were analyzed by their mass spectra, also compared to those of authentic samples.

The stability of the products and the reliability of the esterification and workup procedure were tested by emulating workup conditions with mixtures of authentic samples. The *erythro*-acid and -bromohydrin, individually or together, or their esters, along with excess starting acid or ester, and NaBr in 75% acetic acid were subjected to the workup procedure. There were no substantial changes in the ratios of products found by GLC, and no other products were detected, indicating that the products of the reaction are stable to the workup condition. The duplicate isolation runs (Table II) agreed on the average within ±1.2%. The sensitivity of the GLC procedure was tested by analyzing known mixtures. It was found that 1% of the *erythro*-bromohydrin ester and 1% of the *threo*-dibromo ester could be detected in an excess of the *erythro*-dibromo ester but that 0.5% could not. The same results were observed when the starting materials were the acids, so that no substantial change occurs during the esterification procedure. Authentic samples of the two anti-Markownikoff bromohydrins were not available, but at no time were products observed which could not be completely accounted for by the above compounds.[13,35]

Kinetic Determinations. These were carried out exactly as described before at 25.00 ± 0.05 °C except for those used in the determination of activation parameters.[3] In most cases, kinetic runs were carried to 60–90% completion. Rate constants were calculated with a least-squares program, all runs were conducted in duplicate, and if the discrepancy between duplicate runs was greater than 3% they were repeated. Several runs were also checked by graphing. The least-squares errors in the slopes averaged 0.77% and in the intercepts 0.27%. All quoted errors are probable errors obtained from the least-squares calculations.

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References and Notes

(1) Kinetics of Halogenation of Olefins and Acetylenes. 6. For part 5 in this series, see ref 3.
(2) Taken in part from the Ph.D. Dissertation of S. DeYoung, Bryn Mawr College, May 1976.
(3) S. J. Ehrlich and E. Berliner, *J. Am. Chem. Soc.*, **100,** 1525 (1978).
(4) P. W. Robertson, N. T. Clare, K. J. McNaught, and G. W. Paul, *J. Chem. Soc.*, 335 (1937); I. K. Walker and P. W. Robertson, *ibid.*, 1515 (1939).
(5) The rate constants k_2 are in M^{-1} s^{-1} and k_3 in M^{-2} s^{-1}.
(6) S. DeYoung, S. Ehrlich, and E. Berliner, *J. Am. Chem. Soc.*, **99,** 290 (1977).
(7) J. E. Dubois and F. Garnier, *Tetrahedron Lett.*, 3961 (1965); R. E. Buckles and J. P. Yuk, *J. Am. Chem. Soc.*, **75,** 5048 (1953); G. A. Olah and T. R. Hockswender, Jr., *ibid.*, **96,** 3574 (1974), and references cited therein; M. F. Ruasse and J. E. Dubois, *J. Org. Chem.*, **37,** 1770 (1972); C. G. Gebelein and G. D. Frederick, *ibid.*, **37,** 2211 (1972); G. MOdena, F. Rivetti, and U. Tonellato, *ibid.*, **43,** 1521 (1978).
(8) (a) J. H. Rolston and K. Yates, *J. Am. Chem. Soc.*, **91,** 1469 (1969); (b) **91,** 1477 (1969); (c) **91,** 1483 (1969).
(9) The product distribution in the presence of NaOAc is somewhat obscured by the fact that in these runs the NaBr concentration was also varied, and NaBr increases the amount of dibromide and therefore suppresses sodium acetate or solvent incorporation. See also ref 8b.
(10) D. S. Tarbell and P. D. Bartlett, *J. Am. Chem. Soc.*, **59,** 407 (1937).
(11) P. B. D. de la Mare and R. Bolton, "Electrophilic Additions to Unsaturated Systems", American Elsevier, New York, 1966, p 140.
(12) Reference 8. Also see A. Modro, G. Schmid, and K. Yates, *J. Org. Chem.*, **42,** 3673 (1977); K. Yates and R. S. McDonald, *ibid.*, **38,** 2465 (1973). In the more nucleophilic solvent methanol, more solvent incorporation occurs; see J. E. Dubois and J. R. Chretien, *J. Am. Chem. Soc.*, **100,** 3507 (1978).
(13) J. M. Agoff, M. C. Cabaleiro, and J. C. Podesta, *Chem. Ind. (London)*, 305 (1974); J. M. Agoff and M. C. Cabaleiro, *Tetrahedron Lett.*, 3535 (1975); M. A. Wilson and P. D. Woodgate, *J. Chem. Soc., Perkin Trans. 2,* 141 (1976).
(14) P. B. D. de la Mare and R. Bolton, ref 11, Chapter 7; K. Yates and W. V. Wright, *Tetrahedron Lett.*, 1927 (1965); R. E. Buckles, J. L. Miller, and R. J. Thurmaier, *J. Org. Chem.*, **32,** 888 (1967); G. A. Olah, R. D. Porter, C. L. Jeuell, and A. M. White, *J. Am. Chem. Soc.*, **94,** 2044 (1972).
(15) R. C. Fahey and H.-J. Schneider, *J. Am. Chem. Soc.*, **90,** 4429 (1968).
(16) G. H. Schmid, A. Modro, and K. Yates, *J. Org. Chem.*, **42,** 871 (1977); G. H. Schmid and T. T. Tidwell, *ibid.*, **43,** 460 (1978); G. H. Schmid, *ibid.*, **43,** 777 (1978).
(17) J. A. Pincock and K. Yates, *J. Am. Chem. Soc.*, **90,** 5643 (1968); *Can. J. Chem.*, **48,** 3332 (1970); also ref 3. In iodination: M. H. Wilson and E. Berliner, *J. Am. Chem. Soc.*, **93,** 208 (1971); E. Mauger and E. Berliner, *ibid.*, **94,** 194 (1972); V. L. Cunningham and E. Berliner, *J. Org. Chem.*, **39,** 3731 (1974). In hydrochlorination: R. C. Fahey and D. J. Lee, *J. Am. Chem. Soc.*, **90,** 2124 (1968); *ibid.*, **88,** 5555 (1966).
(18) P. B. D. de la Mare, *Q. Rev. Chem. Soc.*, **3,** 126 (1949); P. B. D. de la Mare and R. Bolton, ref 14; R. C. Fahey, *Top. Stereochem.*, **3,** 237 (1968); R. E. Buckles, J. L. Miller, and R. J. Thurmaier, ref 14; J. E. Dubois and E. Bienvenue-Goetz, *Bull. Soc. Chim. Fr.*, 2086 (1968); J. E. Dubois and X. Q. Huynh, *Tetrahedron Lett.*, 3369 (1971); R. C. Fahey, M. T. Paine, and D. J. Lee, *J. Org. Chem.*, **39,** 1124 (1974).
(19) P. D. Bartlett and D. S. Tarbell, *J. Am. Chem. Soc.*, **58,** 466 (1936).
(20) E. Berliner and M. C. Beckett, *J. Am. Chem. Soc.*, **79,** 1425 (1957); R. P. Bell and E. N. Ramsden, *J. Chem. Soc.*, 161 (1958); R. P. Bell and T. Spencer, *ibid.*, 1156 (1959); R. P. Bell and D. J. Rawlinson, *ibid.*, 63 (1961).
(21) K. Nozaki and R. A. Ogg, Jr., *J. Am. Chem. Soc.*, **64,** 697, 704, 709 (1942).
(22) N. P. Kanyaev, *Zh. Obshch. Khim.*, **29,** 841 (1959).
(23) J. R. Atkinson and R. P. Bell, *J. Chem. Soc.*, 3260 (1963); R. P. Bell and M. Pring, *J. Chem. Soc. B,* 1119 (1966).
(24) P. B. D. de la Mare and R. Bolton, ref 14, p 121.
(25) J. E. Dubois, A. F. Hegarty, and E. D. Bergmann, *J. Org. Chem.*, **37,** 2218 (1972).
(26) R. C. Fahey, M. W. Monahan, and C. A. McPherson, *J. Am. Chem. Soc.*, **92,** 2810 (1970); R. C. Fahey and M. W. Monahan, *ibid.*, **92,** 2816 (1970); R. C. Fahey and C. A. McPherson, *ibid.*, **93,** 2445 (1971); R. C. Fahey, C. A. McPherson, and R. A. Smith, *ibid.*, **96,** 4534 (1974); D. J. Pasto, G. R. Meyer, and B. Lepeska, *ibid.*, **96,** 1858 (1974).
(27) P. B. D. de la Mare and R. D. Wilson, *J. Chem. Soc., Perkin Trans. 2,* 2048, 2055, 2062 (1977).
(28) Rolston and Yates[8] observed that in the bromination of substituted styrenes $\rho_{Br_2} > \rho_{Br_3^-}$ (−4.21 and −2.02, respectively), which they interpret to be consistent with the lower electrophilicity of the tribromide ion *or* an Ad_E3 process, because less charge would be developed at C_α in either process. In the present case, a change of solvent from 75 to 50% aqueous acetic acid increases k_2 by a factor of 7.9 but k_3 by only 4.6, also indicating that less cationic charge is developed in the reaction corresponding to the second term in the rate equation.
(29) K. W. F. Kohlrausch and A. Pongratz, *Monatsh. Chem.*, **64,** 374 (1934).
(30) M. Reimer, *J. Am. Chem. Soc.*, **64,** 2510 (1942).
(31) A. Michael, *Chem. Ber.*, **34,** 3640 (1901).
(32) P. B. D. de la Mare and M. A. Wilson, *J. Chem. Soc., Perkin Trans. 2,* 653 (1973).
(33) J. Read and A. C. P. Andrews, *J. Chem. Soc.*, **119,** 1774 (1921).
(34) We are greatly indebted to Professor P. B. D. de la Mare for supplying us with this sample.
(35) J. J. Sudborough and K. J. Thompson, *J. Chem. Soc.*, **83,** 666 (1903). This acid, conceivably formed by dehydration of one of the bromohydrins, was not found among the reaction products.
(36) T. W. Abbott and D. Althousen in "Organic Syntheses", Collect. Vol. 2, A. H. Blatt, Ed., Wiley, New York, 1943, p 270. The procedure for the bromination of the *ethyl* ester was followed.
(37) C. Lieberman, *Chem. Ber.*, **24,** 1101 (1891).
(38) S. Bagchee, K. N. Gaind, and J. N. Ray, *J. Chem. Soc.*, 657 (1938).

Polymer-Anchored Palladium(II) Complexes as Catalysts for the Conversion of Quadricyclane to Norbornadiene

R. B. King* and R. M. Hanes[1]

Department of Chemistry, University of Georgia, Athens, Georgia 30602

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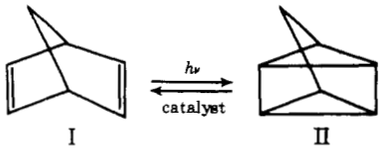
Reaction of diphenylphosphinated macroreticular polystyrene with $(CH_3CN)_2PdCl_2$ gives a polymer-supported palladium(II) chloride which is an active catalyst for the conversion of quadricyclane to norbornadiene. However, the activity of this catalyst is less by factors of 2–85 than that of the soluble catalyst $[(C_6H_5)_3P]_2PdCl_2$. The new polymer-supported palladium catalyst, like previously reported polymer-supported catalysts for this reaction, loses some of its activity upon repeated recycling.

A promising system for the storage of solar energy is based on the photosensitized conversion of norbornadiene (I) to quadricyclane (II) as the energy-storage step followed by the catalyzed exothermic reversion of quadricyclane to norbornadiene as the energy-release step.[2-4] Ideal catalysts for this reversion reaction must meet stringent criteria including long-term stability as well as the ability to effect rapid quantitative conversion with no side reactions. In addition, in an actual energy storage device based on this principle, the catalyst must be immobilized to prevent dispersion of the catalyst throughout the system.



I II

Several catalyst systems are known which catalyze the conversion of quadricyclane (II) to norbornadiene (I). These include soluble complexes of rhodium(I),[5] nickel(II),[6] cobalt(II),[6] iron(II),[6] and palladium(II)[5,7] and the soluble metal dithiolenes[8] $[(CF_3)_2C_2S_2]_2Ni$ and $[(CF_3)_2C_2S_2]_3Mo$. However, most of these complexes do not lend themselves readily to immobilization onto an insoluble polymer. Thus the most

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