Mechanism of Reactions Promoted by Polymer-Supported Phase-Transfer Catalysts

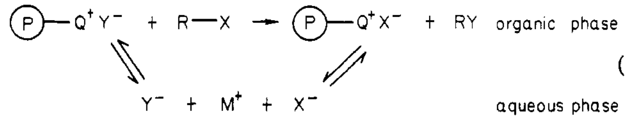
Fernando Montanari,*† Silvio Quici,† and Pietro Tundo‡

Centro CNR and Istituto di Chimica Industriale dell'Università, I-20133 Milano, Italy, and Istituto di Chimica Organica dell'Università, I-10125 Torino, Italy

Received April 14, 1982

Kinetic measurements indicate that the ratio of C- vs. O-alkylation of β-naphthoxide is not a reliable polarity test for polymer-supported phase-transfer catalysis because of the competitive noncatalyzed reactions. A reliable test is the C/O-alkylation of phenoxide. Reactions carried out in toluene–water in the presence of stoichiometric amounts of polystyrene-supported quaternary phosphonium salts **2** and **3** afford only O-alkylation products. Stoichiometric reactions give significant amounts of C-alkylation with **2** or **3** in aqueous ethanol or with immobilized polar catalysts **4** and **5** in toluene–water. Hydration measurements agree with the essentially hydrophobic character of polystyrene-supported phosphonium catalysts **2** and **3**. These results confirm our previous conclusion that phase-transfer catalysis follows identical mechanisms both in the presence of soluble and polymer-supported catalysts. In the latter case the reaction should occur within an organic solvation shell firmly surrounding the catalytic site, rather than in an aqueous solvation sphere or at the interface.

In previous papers[1,2] we put forth the hypothesis that phase-transfer reactions catalyzed by polymer-bonded quaternary onium salts[2,3] followed a mechanism identical with that of classical phase-transfer reactions catalyzed by soluble quaternary salts. The reactions should occur in the organic shell surrounding the catalytic site as described in eq 1. Anions are exchanged at the water–organic solvent interface, and in both the aqueous and organic liquid phases charge parity is provided by the inorganic cation M^+ and the polymer-supported quaternary cation Q^+, respectively.[1,2]

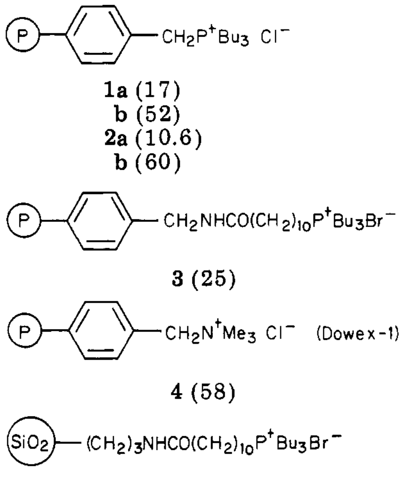


(1)

However, in very recent studies, Regen and co-workers arrived at completely different conclusions.[4a] They used quaternary phosphonium chloride groups bonded to microporous 1% cross-linked polystyrene, with 17% (**1a**) and 52% (**1b**) ring substitution (Chart I), as phase-transfer catalysts.[4a,b] On the basis of the results obtained in nucleophilic substitution reactions carried out in the presence of **1a** and **1b**, they concluded that in the immobilized catalyst, the pendant ions form inverted micelles encased in the polymer matrix; as in micelle chemistry, reactions should substantially occur at the organic solvent–water interface. These conclusions were supported by measurements of imbibed solvents, by the C/O-alkylation ratio of β-naphthol and by ^{13}C NMR spectra measured under triphase conditions. Unlike **1a**, **1b** afforded mainly C-alkylation product **6** in the reaction beteween β-naphthoxide and benzyl bromide. In the reaction between chloride ion and *n*-decyl methanesulfonate, the reactivity of **1a**, as well as the amount of water or organic solvent imbibed, strongly depended on the salt concentration in the aqueous phase.[4a]

It is well-known that the C/O-alkylation ratio of phenols or naphthols is related to the specific solvation of $Ar-O^-$ in the reaction medium; polar solvents favor C-alkylation, whereas aprotic anion-unsolvating solvents lead to O-alkylation products.[5] Therefore, almost only O-alkylation has always been observed in classical phase-transfer catalysis,[6] where reactions occur in the nonpolar organic phase.[2]

Chart I[a]

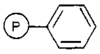


1a (17)
b (52)
2a (10.6)
b (60)

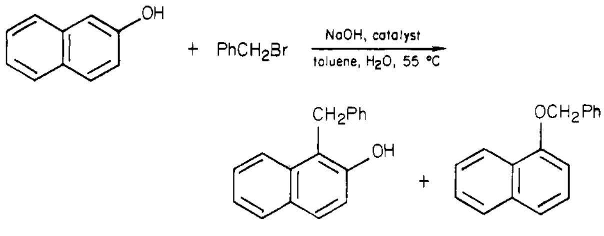
3 (25)

4 (58)

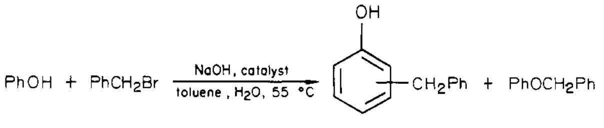
5

[a]  = microporous polystyrene, 1% cross-linked with *p*-divinylbenzene(percent ring substitution in parentheses).

In the present paper we have studied alkylation reactions of β-naphthol and phenol (eq 2 and 3) in the presence



6 **7** (2)



8 **9** (3)

---

† Centro CNR and Milano University.

‡ Torino University.

[1] Molinari, H.; Montanari, F.; Quici, S.; Tundo, P. *J. Am. Chem. Soc.* **1979**, *101*, 3920–3927.

[2] Montanari, F.; Landini, D.; Rolla, F. In "Host Guest Complex Chemistry II"; Vogtle, F., Ed.; Springer-Verlag: West Berlin, 1982; *Top. Curr. Chem.* **1982**, *101*, 147–200.

Table I. Observed Pseudo-First-Order Kinetic Constants for C-Alkylation (k_C) and O-Alkylation (k_O) of β-Naphthoxide with Benzyl Bromide under Phase-Transfer Conditions in the Presence of Polymer-Supported Catalysts[a]

catalyst[b]	% ring substitution	10^5k_{obsd}, s^{-1}		
		k_C	k_O	k_{alk}
		8.7	1.6	10.3
2a	10.6	3.0	7.7	10.7
2b	60.0	3.5	5.6	9.1
3	25.4	3.4	8.6	12.0
4	58.0	8.7	2.4	11.1

[a] A 0.2 M solution of $PhCH_2Br$ in toluene; 1.75 molar equiv of β-naphthol in a 0.2 N NaOH aqueous solution, stirring speed 1300 rpm at 55 °C. [b] 0.1 molar equiv.

Table II. Observed Pseudo-First-Order Kinetic Constants and Product Distribution for the Alkylation Reaction of Phenoxide with Benzyl Bromide under Phase-Transfer Conditions in the Presence of Polymer-Supported Catalysts[a]

catalyst[b]	10^4k_{obsd}, s^{-1}	product distribution, %	
		8	**9**
	0.32	22	78
2a	9.7	0	100
2b	5.4	0	100
3	9.5	0	100
4	0.37	8.6	91.4

[a] A 0.2 M solution of $PhCH_2Br$ in toluene; 1.75 molar equiv of phenol in a 0.2 N NaOH aqueous solution; stirring speed 1300 rpm at 55 °C. [b] 0.2 molar equiv.

Table III. Product Distribution in the Alkylation Reaction of β-Naphthoxide with Benzyl Bromide in the Presence of Stoichiometric Amounts of Polymer-Supported Quaternary Salts[a]

supported quaternary salt[b]	product distribution, %			
	phase-transfer conditions		EtOH-H_2O[c]	
	6	**7**	**6**	**7**
2a	0	100	5.5	94.5
2b	0	100	7.6	92.4
3	0	100	5.5	94.5
4	44	56		
5	15	85		

[a] A 0.2 M solution of $PhCH_2Br$ in toluene; 1 molar equiv of β-naphthol in a 0.2 N NaOH aqueous solution; stirring speed 1300 rpm at 55 °C. [b] 1 molar equiv. [c] 1.5:1 v/v.

of a series of immobilized catalysts (**2**–**5**) having different structural features. Among these catalysts, phosphonium salts **2a** and **2b**, bonded to 1% cross-linked polystyrene and with 10.6% (**2a**) and 60% (**2b**) ring substitution, were closely related to **1a** and **1b**, respectively. We also included in our study the following: phosphonium salt **3**, in which tributylphosphonium groups are bonded to 1% cross-linked polystyrene matrix (25% ring substitution) through a 13-atom linear chain; the commercial resin **4** (Dowex-1) which is 1% cross-linked polystyrene bearing $CH_2N^+Me_3Cl^-$ groups with 58% ring substitution; phosphonium salt **5** supported on silica gel.[7]

We initially examined C/O-alkylation of β-naphthoxide with benzyl bromide in the presence of **2a** and **2b** under conditions substantially identical with those described by Regen (toluene–water for 18 h at 50 °C without stirring). With catalytic amounts of **2a** and **2b** (0.10 mequiv), 34% and 32% conversions were obtained, respectively, and in both cases the reactions afforded a 1:3 ratio of C-alkylated, **6**, and O-alkylated, **7**, products. By using stoichiometric amounts of **2a** and **2b** under identical reaction conditions 50% and 41% conversions were observed, respectively, but in both cases O-alkylated derivative **7** was the only product. In agreement with Regen's data was the control experiment carried out in the absence of catalyst, which afforded a 1:5 ratio of **6** and **7** with 9% total conversion.

Due to the impossibility of reproducing Regen's data in catalyzed reactions, we carried out kinetic measurements in order to obtain more precise information on the microenvironment of catalytic site and therefore on the mechanism of phase-transfer reactions promoted by polymer-bonded catalysts. The kinetics of alkylation of β-naphthol in toluene–water at 55 °C was followed by measuring the formation rate of both C-alkylated product **6** (k_C), and of O-alkylated product **7** (k_O). Results are reported in Table I. They show similar k_{alk} ($k_{alk} = k_C + k_O$) values for polystyrene-supported phosphonium salts, slightly decreasing in the order **3** > **2a** > **2b**; in these three cases k_O is always greater than k_C by a factor of 1.6–2.6. The reaction repeated in the absence of catalyst gave a k_{alk} value comparable to that of catalyzed reactions, but the k_C/k_O ratio was inverted, with k_C being 5 times greater than k_O. The observed k_C and k_O in the presence of catalysts **2** and **3** are not the true rate constants since the noncatalyzed reactions are competitive. The influence of the latter reactions evidently depends on various factors difficult to evaluate quantitatively, such as the interface area of the two liquid phases and hence the speed and the mode of stirring, etc.[8]

In the presence of **4** (Dowex-1 commercial resin), which is much more polar and hydrophilic than **2** and **3**, the results were very similar to those of the reaction carried out in the absence of catalyst. C-alkylation products were isolated in 30–40% yields in reactions catalyzed by **2** and **3**. The yield rose to 80% in the presence of **4** and in the noncatalyzed reaction. Experiments in the presence of 5 instead of 10 molar % of polymeric catalyst gave very similar values.

Alkylation rates were also measured, under similar conditions, by using phenol instead of β-naphthol (Table II); however, in this case the k_{alk} observed in catalyzed reactions (0.2 molar equiv of catalyst) were 30 times higher than those found in the absence of catalyst. Resins **2** and **3** afforded exclusively the O-alkylation product **9**, whereas in the noncatalyzed reaction C-alkylated product **8** was obtained in 22% yield. With resin **4** k_{alk} was very low and similar to that of the noncatalyzed reaction; in this case C-alkylated product was isolated in 8.6% yield.

Alkylation of β-naphthol was repeated in the presence of stoichiometric amounts of polymeric catalyst. In the

---

(3) (a) Regen, S. L. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 421–429. (b) Sherrington, D. C. In "Polymer-Supported Reactions in Organic Synthesis"; Hodge, P., Sherrington, D. C., Eds.; Wiley: New York, 1980; pp 180–194. (c) Chiellini, E.; Solaro, R.; D'Antone, G. *Makromol. Chem. Suppl.* **1981**, *5*, 82–106.

(4) (a) Ohtani, N.; Wilkie, C. A.; Nigam, A.; Regen, S. L. *Macromolecules* **1981**, *14*, 516–520. (b) Ohtani, N.; Regen, S. L. *Ibid.* **1981**, *14*, 1594–1595.

(5) Kornblum, N.; Seltzer, R.; Haberfield, P. *J. Am. Chem. Soc.* **1963**, *85*, 1148–1154. (b) Reutov, O. A.; Kurts, A. C. *Russ. Chem. Rev. (Engl. Transl.)* **1977**, *46*, 1040–1056.

(6) D'Incan, E.; Viout, P. *Tetrahedron* **1975**, *31*, 159–164.

(7) (a) Tundo, P.; Venturello, P. *J. Am. Chem. Soc.* **1979**, *101*, 6606–6613. (b) *Ibid.* **1981**, *103*, 856–861.

(8) Carrying out the reaction in the absence of stirring does not modify the essence of the problem, since the competition with the noncatalyzed reactions still depends on the interface area, and various experiments[3a,9] indicate that the latter may substantially increase in the presence of the polymeric catalyst.

(9) Regen, S. L.; Besse, J. J. *J. Am. Chem. Soc.* **1979**, *101*, 4059–4063.

three cases (Table III), catalysts **2a**, **2b**, and **3** afforded exclusively **7**. Resin **4** and silica-bound phosphonium salt **5**, on the contrary, gave 44% and 15% of C-alkylated product **6**, respectively.

When resins **2a,b** and **3** were reacted with stoichiometric amounts of β-naphthoxide and benzyl bromide in ethanol–water (1.5:1 v/v), the observed C-alkylation was between 5.5% and 7.5%, with the highest value obtained with resin **2b**.

Other experiments were concerned with the hydration of polymeric catalysts **2–5** as a function of the structure and percent ring substitution in the matrix. Catalysts **2a,b** and **3** were equilibrated with a saturated aqueous solution of alkaline halides and toluene. After filtration and being allowed to stand 2–3 h at room temperature, they reached a constant weight. The amounts of water absorbed and of halides present were measured by Karl-Fischer and potentiometric titrations, respectively. The water–halide ratios ranged between 1.7 and 3.2 and corresponded to the hydration numbers found[10] for quaternary onium salts dissolved in the organic phase under standard phase-transfer catalysis conditions.

Although these numbers vary with the anion, they are independent of the cations[1,2] and are identical with those previously found[1] for similar polymer-supported quaternary salts: in particular, no difference was found between catalysts **2a** and **2b** with a low and high degree of substitution, respectively.

When resin **4** was similarly equilibrated under phase-transfer conditions, 72 h of standing at room temperature was required for a filtered sample to reach a constant weight. In any case, the final H_2O/Cl^- ratio was 3.15, still similar to those found for resins **2** and **3**.

A final comment concerns the comparison of C/O-alkylation and hydration data with ^{13}C NMR measurements,[4a] which lead to contradictory conclusions. In this respect it has to be observed that in the absence of measurements with rapid spinning of the sample about an axis inclined at the magic angle (MAR-NMR), ^{13}C NMR spectral resolution may be affected not only by the mobility of pendant groups in the microenvironment but also by the anisotropy of magnetic susceptibility caused by simple physical heterogeneity of the sample.[11] This might be expecially true in the presence of two immiscible liquid phases.

The results obtained in the present paper indicate the following. (i) The C/O-alkylation ratio of β-naphthoxide, due to the competition with the noncatalyzed reactions, cannot give any quantitative indication of the microenvironment of phase-transfer reactions in the presence of catalytic amounts of polymer-bonded catalyst. However, this measurement applied to phenol is a valid test since the uncatalyzed reactions are very slow. (ii) An increase of polarity around the catalytic site, which certainly occurs when the percent of ring substitution is increased, i.e., passing from **2a** to **2b** (or from **1a** to **1b**), does not influence the C/O-alkylation ratio, although in some instances it can give rise to a marked decrease of nucleophilic substitution rates.[12,13] (iii) Alkylation of β-naphthol in the presence of stoichiometric amounts of polymer-supported quaternary salts **2** and **3** excludes any possibility of interference with the noncatalyzed reaction: the observation of O-alkylation only implies that the reaction occurs in a nonpolar organic medium.[1] In agreement with these results, stoichiometric reactions carried out with **2** and **3** in polar homogeneous media (aqueous ethanol) or with highly hydrophilic and polar catalysts, like **4** and **5**, in a toluene–water two-phase system, afford significant amounts of C-alkylation products. (iv) Easy elimination of imbibed water from the filtered catalyst shows the essentially hydrophobic character of tributylalkylphosphonium salts bonded to the polystyrene matrix; the only water firmly retained by the polymer is that of the anion hydration sphere in nonpolar organic phases. The much greater hydrophilicity of resin **4** is shown by the much longer time required for the spontaneous evaporation at room temperature of water not involved in the specific solvation of the anion. (v) As in classical phase-transfer catalysis, reactions follow pseudo-first-order kinetics: it was previously found by us[1] and by other authors[9,15] that the observed rate constants are linearly dependent on the molar equivalents of the polymer-supported catalyst.

Efficient polymer-supported and soluble phase-transfer catalysts should satisfy analogous structural requirements; in particular, for quaternary onium salts, substituents should provide a high lipophilic character and a topology allowing sufficient separation between the anion and the cationic center.[1] When these requirements are satisfied, anion activation in conventional phase-transfer catalysis in the presence of soluble quaternary salts is comparable to or greater than the anion activation in dipolar aprotic solvents.[10a,16] In the case of polymer-supported catalysts, diffusive factors[1-3,15] or a high polarity around the catalytic center[7,12,13] can substantially decrease the reaction rates; when these factors are suitably minimized, the reactivity of polymer-bound catalysts having an optimal structure is only slightly lower than that observed with similar soluble catalysts.[1,13]

These results are consistent with our previous hypothesis[1,2] that reactions proceed with identical mechanisms under phase-transfer conditions both in the presence of soluble and polymer-supported catalysts. Polymer-supported catalyzed reactions should occur within an organic solvation shell firmly surrounding the catalytic site, rather than in an aqueous solvation sphere or at the interface.

Experimental Section

General Methods. Catalysts **2a,b** and **3** were prepared as previously described[1] from commercially available chloromethylated polystyrene (Fluka A.G.) cross-linked with 1% *p*-divinylbenzene having 1.04, 5.0, and 2.63 mequiv of Cl/g. Silica gel supported catalyst **5** was synthesized by following the previously reported procedure.[7] GLC analyses were performed on a Hewlett-Packard Model 5840 flame-ionization instrument (2 ft × 0.125 in. UCW 982 on Chromosorb W column at 160 °C) and on a Varian 1400 instrument with columns of 5% SE-30 on Varaport at 150–250 °C. Hydration-state measurements were carried out on a Microhm Karl-Fisher Automat-547 instrument with a Model 645 Multi-Dosimat. Organic and inorganic reagents were ACS reagent grade.

C/O-Alkylation of β-Naphthoxide and Phenoxide in the Absence of Stirring. Catalysts **2a** and **2b** (40 and 8.8 mg, respectively, 0.02 mequiv), 1 mL of a 0.2 M aqueous solution of sodium β-naphthoxide, 1 mL of a 0.2 M toluene solution of benzyl bromide, and 0.02 mmol of octadecane as an internal standard

---

(10) (a) Landini, D.; Maia, A.; Montanari, F. *J. Am. Chem. Soc.* **1978**, *100*, 2796–2801. (b) *J. Chem. Soc., Chem. Commun.* **1977**, 112–113.

(11) Doskocilova, D.; Schneider, B. *Pure Appl. Chem.* **1982**, *54*, 575–584.

(12) Regen, S. L.; Bolikal, D.; Barcelon, C. *J. Org. Chem.* **1981**, *46*, 2511–2514.

(13) Montanari, F.; Quici, S., unpublished results.

(14) Unlike the corresponding chloride,[4a] the partition values were 120:1 in toluene–water for $PhCH_2P^+Bu_3$-β-$C_{10}H_7O^-$ (see Experimental Section).

(15) (a) Tomoi, M.; Ford, W. T. *J. Am. Chem. Soc.* **1981**, *103*, 3821–3828. (b) *Ibid.* **1981**, *103*, 3828–3832.

(16) Landini, D.; Maia, A.; Montanari, F. *Nouv. J. Chem.* **1979**, *3*, 575–577.

were placed in a test tube with a diameter of 10 mm equipped with a Teflon-lined screw cap. The reaction mixture was handly shaked for 1 min and then kept at 50 °C for 18 h in a thermostat. After addition of 1 mL of 0.2 N aqueous HCl and extraction with $CHCl_3$ (3 × 10 mL), the organic layer was separated and analyzed by GLC. The reaction was repeated under identical conditions by using stoichiometric amounts of **2a** and **2b** (400 and 88 mg, respectively) and in the absence of catalyst. The data reported in the text are not corrected for the uncatalyzed reaction.

Kinetic Measurements. Kinetics were run in a cylindric 50-mL flask (internal diameter 3.0 cm) equipped with a Teflon-lined screw cap and thermostated at 55 °C with circulating butyl phthalate and a magnetic stirrer (2.5 cm long). The temperature was controlled to within ±0.02 °C by a Colora K-5 ultrathermostat. The stirring speed (1300 ± 50 rpm) was controlled by using a strobe light. A general example of the procedure employed follows. The flask was charged with 202 mg (1.4 mmol) of β-naphthol, 7 mL of 0.2 N aqueous sodium hydroxide, 20 mg (0.0786 mmol) of octadecane as an internal standard, 2 mL of toluene, and 80 mg (0.08 mequiv) of resin **3** (1 mequiv of Br^-/g, 25% ring substitution). The mixture was stirred at the reaction temperature for 3 h to condition the catalyst. Benzyl bromide (2 mL of a 0.4 M toluene solution) was added at zero time. The reaction was followed by GLC analysis up to about 40% conversion, after which a progressive deviation from the pseudo-first-order stright lines was observed both for products **6** and **7**. The pseudo-first-order rate constants (k_C and k_O) were obtained by following ln [**6**] and ln [**7**] vs. time and computed by the least-square method. The measurements were repeated at least twice, and their reproducibility was found to be ±10%.

Product Distribution in the Alkylation of β-Naphthoxide with Equimolecular Amounts of Polymer-Supported Quaternary Salts. A 50-mL flask was charged with 72 mg (0.5 mmol) of β-naphthol, 2.5 mL of aqueous 0.2 N sodium hydroxide (0.5 mmol), and 0.5 g of resin **3** (0.5 mequiv) and heated at 55 °C for 2 h with magnetic stirring. Benzyl bromide (2.5 mL) of a 0.2 M toluene solution) was added, and heating and stirring were continued for 18 h. The reaction mixture was acidified with 2 mL of 2 N aqueous hydrochloric acid, 5 mL of toluene was added, and the organic phase was analyzed by GLC in the presence of octadecane as an internal standard.

Hydration State of Polymeric Catalysts. The catalyst was stirred for 3 h at 90 °C in the presence of toluene and saturated aqueous solution of sodium or potassium halide; after filtration and being allowed to stand at room temperature, it reached a constant weight after 2–3 h for catalysts **2a,b** and **3** and after 72 h for catalyst **4**. Karl-Fisher and potentiometric titrations on weighed portions of catalyst, carried out as previously reported,[1] gave the amounts of absorbed water and halide ions, respectively. The H_2O/Br^- and H_2O/Cl^- ratios were 1.7 and 2.8–3.2 for catalysts **3**, and **2a,b**, and **4**, respectively.

Distribution of Benzyltributylphosphonium β-Naphthoxide in a Toluene-Water Two-Phase System. A solution of the quaternary salt (436 mg, 1 mmol) in 2 mL of toluene and 2 mL of water was stirred for 2 h at room temperature. A measured portion (1.0 mL) of the organic phase was added to 1.0 mL of water, 1.0 mL of 1 N HCl, and 1.0 mL of ethyl ether (solution A). A measured portion (1.0 mL) of the aqueous phase was added to 1.0 mL of toluene, 1.0 mL of 1 N HCl, and 1 mL of ethyl ether (solution B). Both solutions were shaken, and the amount of β-naphthol in the organic portions of A and B was determined by GLC (SE-30 on Varaport-5%, 180 °C). The A/B ratio was 120.

Acknowledgment. This paper was supported by a grant from the "Progetto Finalizzato di chimica fine e secondaria" of Consiglio Nazionale delle Ricerche (CNR) Roma.

Registry No. Dowex-1, 11138-21-9; sodium β-naphthoxide, 875-83-2; sodium phenoxide, 139-02-6; benzyl bromide, 100-39-0; benzyltributylphosphonium β-naphthoxide, 83746-97-8.

Multipathway Mechanism in Aryl Olefin Bromination: Competition between Tertiary and Secondary Carbocation Pathways

Marie-Françoise Ruasse* and Alain Argile

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

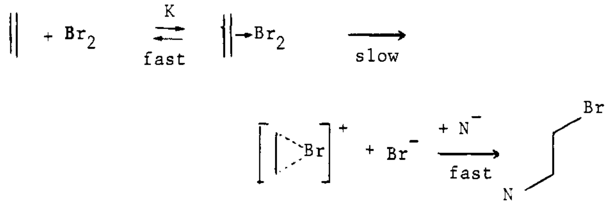
Received March 2, 1982

Rate constants, product stereochemistry, and regiochemistry of the bromination of 26 α-methylstilbenes $XC_6H_4C(Me){=}CHC_6H_4Y$ have been measured in methanol at 25 °C. Kinetic substituent effects on the rate show the competitive formation of secondary and tertiary carbocations in the rate-determining step. The secondary pathway competes with the tertiary one only if Y is strongly electron donating and X electron accepting. The ρ values are all consistent with carbocationic transition states: in the tertiary pathway ρ_α for X is −4.59 and ρ_β for Y is −1.66, whereas in the secondary pathway ρ_β for X, which varies with Y from −1.95 (Y = 4-OMe) to −0.89 (Y = 4-NMe_2), is in the expected range for a β effect. Product analysis is in complete agreement with the kinetic results. The formation of dibromides and methoxy bromides is nonstereoselective as expected from the absence of bromine bridging in the transition states and the intermediates. The experimental regiochemistry is correctly predicted by the relative rates of formation of the secondary and tertiary carbocations. From this rate–product correlation, the first established for an addition reaction, the unambiguous conclusion is that the positive charge distribution does not change on going from the rate-determining to the product-determining transition state.

Though the general Ad_ECl mechanism for the electrophilic addition of bromine to double bonds, postulated by Dubois and Garnier[1] (Scheme I), is now well established, there is still controversy about the structure of the ionic intermediates and of the rate- and product-determining transition states.

This debate is based on the apparently contradictory results given by kinetics and product stereochemistry. Two different approaches have been used to interpret the data.

Scheme I



Schmid et al.[2] postulate that the structures of the transition states of the rate-determining electrophilic step

---

[1] Garnier, F.; Dubois, J. E. *Bull. Soc. Chim. Fr.* **1968**, 3797–3803.