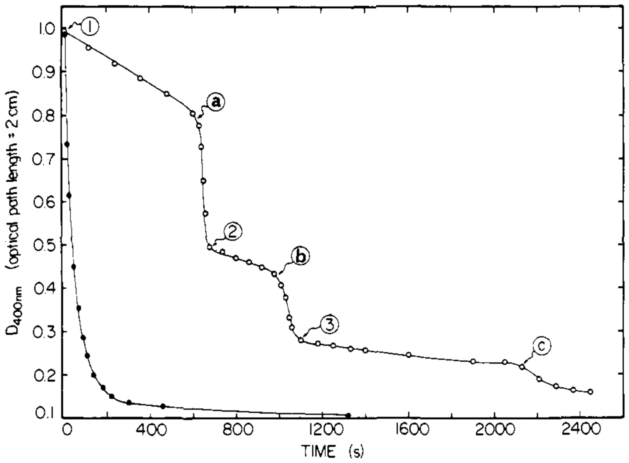


Figure 2. Illustrating the effects of incremental additions of iron(II) ion on the rate of reaction of $CrCH(CH_3)_2^{2+}$ with O_2. The runs shown (○) had $[CrR^{2+}]_0 = 0.95 \times 10^{-3}$ M and $[O_2]_0 = 1.1 \times 10^{-3}$ M (held constant by continuous bubbling). At the three points designated by arrows 1–3, Fe^{2+} was injected; the concentrations (M × 10^3) of Fe^{2+} and $CrCH(CH_3)_2^{2+}$ at these points are, respectively, (1) 0.58, 0.95; (2) 0.28, 0.51; (3) 0.27, 0.29. Points marked a, b, and c are presumably the times at which the inhibiting Fe^{2+} has been consumed, permitting resumption of the rapid chain reaction. For comparison, the continuously decreasing trace (●) shows the steady reaction at approximately the same initial concentration, 1.0×10^{-3} M CrR^{2+}, without added iron(II).

cation has not been identified among the products, it is postulated to react rapidly with H_3O^+ to produce the ultimate products. Considering what is known about the acid decomposition of the cobalt analogue in both nonaqueous[8a] and aqueous[8b] solutions, formation of acetone is readily accounted for by the reaction

$$(H_2O)_5CrOOCH(CH_3)_2^{2+} + H^+ \rightarrow Cr(H_2O)_6^{3+} + (CH_3)_2C{=}O \quad (5)$$

We postulate that the peroxochromium complex, unlike its cobaloxime analogue, is susceptible to internal oxidation-reduction. Such processes are invoked to account for the minor products, $HCrO_4^-$ and 2-propanol, and constitute reasonable chemistry for this species considering other Cr(III)-peroxide reactions.[9] The unavailability of this species for direct study and observation greatly limits further conclusions concerning its reactivity.

Using an estimate for k_1 ($<10^{-6}$ s^{-1}, based on our observation that homolytic scission[1] fails to occur in preference to acidolysis[10] in the presence of other mild oxidants) and the value[11] $2k_4 = 3 \times 10^6$ dm^3 mol^{-1} s^{-1}, the estimated value of k_3 is $\sim 10^6$ dm^3 mol^{-1} s^{-1}, consistent with this reaction being sufficiently rapid to act as a propagating step. The expression for the chain length from this mechanism is

$$\frac{k_3(k_1/2k_4)^{1/2}[CrCH(CH_3)_2^{2+}]^{3/2}}{k_1[CrCH(CH_3)_2^{2+}]}$$

which corresponds to a chain length of 19 000 at $[CrR^{2+}] = 10^{-3}$ M.

Addition of Fe^{2+} prior to or during the reaction produces a dramatic lowering of rate, which we attribute to its chain-breaking reaction with the propagating isopropylperoxy radical:[12]

$$Fe^{2+} + \cdot OOCH(CH_3)_2 \overset{H^+}{=} Fe^{3+} + (CH_3)_2C{=}O + H_2O \quad (6)$$

Provided that iron(II) is added at a concentration less than that of the organochromium cation, the rapid chain reaction will then resume after a substantial subsequent period during which Fe^{2+} is oxidized. Injection of small quantities of Fe^{2+} throughout the reaction gives rise to repeated interruption and reinitiation of the main reaction as shown in Figure 2. During the interrupted segments, the remaining rate is some three-four times faster than the nonradical spontaneous acidolysis, $CrCH(CH_3)_2^{2+} + H_3O^+ = Cr^{3+}_{aq} + C_3H_8$, suggesting that reaction 6 competes favorably but not exclusively with the chain-propagation step. Owing to these factors, the rate during the inhibition period does not provide an independent measure of k_1.[5,13]

The chain mechanism in reactions 1–4 bears a strong resemblance to that claimed in other systems,[14-16] particularly the autoxidation of organoboranes.[17] The results reported here appear to be the first indication of such processes in organochromium chemistry,[18] however, and may be of broader relevance in considerations of the homogeneous activation of molecular oxygen.[19]

Acknowledgment. This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Chemical Sciences Division. We are grateful to Dr. D. C. Johnson for guidance in the electrochemical method for oxygen determinations.

References and Notes

(1) R. S. Nohr and J. H. Espenson, *J. Am. Chem. Soc.*, **97**, 3392 (1975).
(2) J. P. Leslie II and J. H. Espenson, *J. Am. Chem. Soc.*, **98**, 4839 (1976).
(3) E. W. Abel, J. M. Pratt, R. Whelan, and P. J. Williamson, *S. Afr. J. Chem.*, **30**, 1 (1977).
(4) Determined by gas chromatography. We are grateful to Mr. John Richard and the Ames Laboratory analytical services group for major assistance with the GC determinations.
(5) We acknowledge a referee's suggestion on this point.
(6) A different radical species, $Cr\dot{C}(CH_3)_2^{2+}$, might be the key chain-carrying intermediate.[5] Homolysis of the C–H bond seems a less likely initiation step than that given by eq 1, although both lead to the same rate law. An experiment[5] with deuterium labeling would help, but the necessary hydroperoxide precursor, $(CH_3)_2CDC(CH_3)_2OOH$, is not readily available.
(7) C. Fontaine, K. N. V. Duong, C. Merienne, A. Gaudemer, and C. Gianotti, *J. Organomet. Chem.*, **38**, 167 (1972).
(8) (a) C. Bied-Charreton and A. Gaudemer, *Tetrahedron Lett.*, 4153 (1976); (b) J.-T. Chen and J. H. Espenson, unpublished work.
(9) A. C. Adams, J. R. Crook, F. Bockhoff, and E. L. King, *J. Am. Chem. Soc.*, **90**, 5761 (1968).
(10) M. P. Hyde and J. H. Espenson, *J. Am. Chem. Soc.*, **98**, 4463 (1976).
(11) J. A. Howard in "Organic Free Radicals", W. A. Pryor, Ed., American Chemical Society, Washington, DC, 1978, p 428; this applies to hydrocarbon solvents, and we are assuming the same value for aqueous solution.
(12) K. A. Ingold, *Acc. Chem. Res.*, **2**, 1 (1969), reports analogous reactions for Co^{2+} and Mn^{2+}.
(13) Attempts[5] to use galvinoxyl, a known and efficient scavenger of peroxy radicals in hydrocarbon solvents, in place of Fe^{2+} was frustrated by its direct reaction with the isopropylchromium cation in acetone–water.
(14) C. A. Walling, "Free Radicals in Solution", Wiley, New York, 1957, pp 397–466.
(15) J. A. Howard in "Free Radicals", Vol. II, J. K. Kochi, Ed., Wiley, New York, 1973, pp 3–62.
(16) A. G. Davies in "Organic Peroxides", Vol. II, D. Swern, Ed., Wiley, New York, 1971, Chapter IV.
(17) A. G. Davies and B. P. Roberts, *Chem. Commun.*, 298 (1966); *J. Chem. Soc. B*, 17 (1967).
(18) R. P. A. Sneeden, "Organochromium Compounds", Academic Press, New York, 1975.
(19) J. E. Lyons in "Fundamental Research in Homogeneous Catalysis", M. Tsutsui and R. Ugo, Eds., Plenum Press, New York, 1977.

Debra Ann Ryan, James H. Espenson*
Ames Laboratory and Department of Chemistry
Iowa State University, Ames, Iowa 50011

Received September 19, 1978

A Novel Phase Transfer Catalyst Capable of Facilitating Acid-Catalyzed and/or Electrophilic Reactions

Sir:

Since the beginning of the 1970s, phase transfer catalysis (PTC)[1,2] has rapidly developed as a synthetic technique. Indeed, the development of and the interest in PTC is as widespread in industrial circles as in the academia. The general

0002-7863/79/1501-2489$01.00/0

Table I. Rates of Hydrolysis of *p*-Nitrophenyl Acetate in Two-Layer Aqueous-Organic Systems, with and without Phase Transfer Catalysts

rxn	aqueous layer[a]	organic layer[a]	catalyst[b]	stirring rate, rpm	$10^2 k_{obsd}$, s^{-1}
a	1.5 N HCl	cyclohexane	sodium tetraphenylborate	600	1.81
b	1.5 N HCL	cyclohexane	none	600	0.00[c]
c	1.5 N NaOH	cyclohexane	tetraphenylphosphonium bromide	600	5.60
d	1.5 N NaOH	cyclohexane	none	600	0.59

[a] Volume, 60 mL. [b] Catalyst concentration in reaction a, 0.04 M in the aqueous layer; in reaction b, 0.0022 M in the aqueous layer. [c] No reaction was observed after 48 h of stirring.

Table II. A Comparison of the Equivalents of Acid and Base Extracted into Cyclohexane[a]

aqueous layer[b]	organic layer[b]	catalyst	mequiv/L, H^+	mequiv/L, OH^-
3 N HCl	cyclohexane	sodium tetraphenylborate[c]	6.00	
3 N NaOH	cyclohexane	tetraphenylphosphonium bromide[d]		$\ll 0.01$
3 N NaOH	cyclohexane	tetrabutylphosphonium bromide[c]		<0.01

[a] Equal volumes of aqueous and organic solvent (with desired catalyst) were stirred at 600 rpm for 2 min. Phases were allowed to separate for 35 min; 5 mL of the organic layer was removed and back-titrated for either H^+ or OH^-. [b] 25 mL. [c] 0.1 M in the aqueous layer. [d] Saturated solution in the aqueous layer.

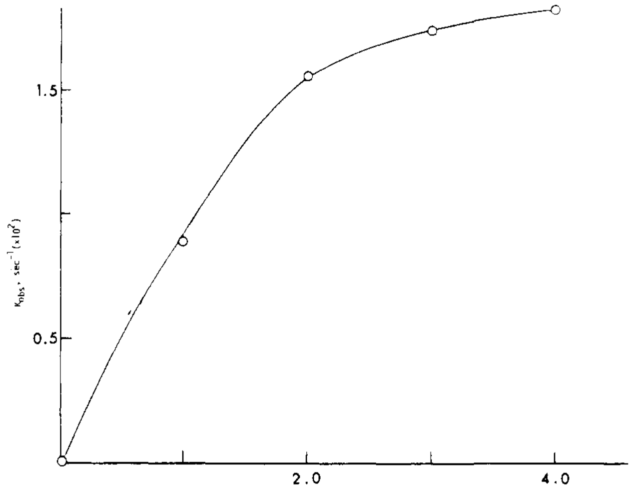


Figure 1. A plot of the rate of hydrolysis (k_{obsd}, s^{-1}) of *p*-nitrophenyl acetate vs. sodium tetraphenylborate concentration in an acidic phase transfer system: organic layer, cyclohexane; aqueous layer, 1.5 N HCl.

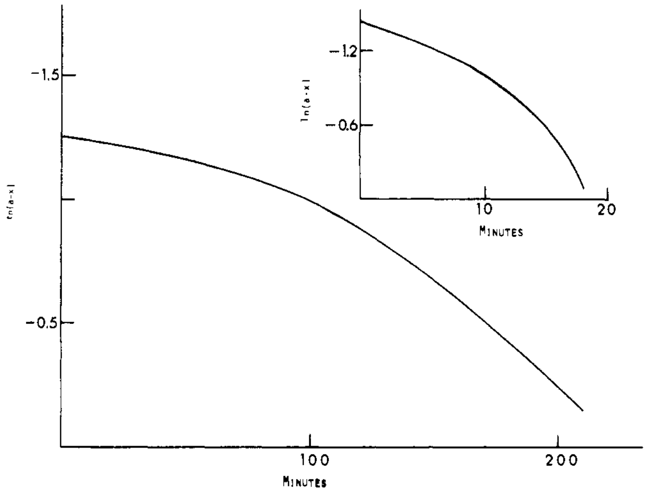


Figure 2. A first-order plot of the disappearance of *p*-toluenesulfonyl chloride vs. time in a two-layer (aqueous-organic) system: organic layer, cyclohexane; aqueous layer, distilled water. The insert graph shows a rate plot for the identical reaction with a phase transfer catalyst (sodium tetraphenylborate) added. Although both appear to be autocatalytic, the reaction with the phase transfer catalyst is much more rapid.

utility and advantages of PTC are well documented.[3-7] All known phase transfer catalysts have two properties in common: (1) they contain hydrophobic alkyl or aryl groups; (2) they are only able to transfer anionic reagents to (or into) organic solvents.[8,9] Consequently the usefulness of PTC is limited to reactions involving anions (i.e., nucleophilic or base-mediated reactions). In this communication an acid-catalyzed hydrolysis, using the first reported "negatively charged" phase transfer catalyst, is described.[10] It is believed that this and other analogous phase transfer catalysts will greatly expand the usefulness of PTC, as acid-mediated and/or electrophilic reactions can be done for the first time via this technique.

The hydrolysis of *p*-nitrophenyl acetate in aqueous-organic two-layer systems was examined.[11] In Table I the rate of the acid-mediated PTC reaction (with and without the sodium tetraphenylborate catalyst) is compared with that of a traditional base-mediated PTC reaction (with and without the tetraphenylphosphonium bromide catalyst). It is interesting that, in the absence of any catalyst, *p*-nitrophenyl acetate (in a two-layer aqueous–organic system) will hydrolyze in the presence of aqueous NaOH but not in the presence of aqueous HCl. For hydrolysis to occur in the acid system one must extract hydronium ion (or some hydrated species thereof, $H_5O_2^+$, $H_7O_3^+$, etc.) sufficiently into the organic layer to react with *p*-nitrophenyl acetate. The tetraphenylborate anion appears to do just that (Table I, a). With a catalytic amount of sodium tetraphenylborate a reaction, which did not occur after 48 h, was complete in <120 s.[12] As expected the addition of a traditional "onium" catalyst to the base system resulted in a substantial rate acceleration as well.

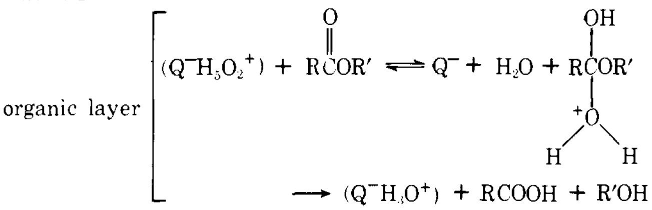
It has been shown that it is difficult to extract appreciable amounts of hydroxide ion into organic solvents with traditional phase transfer catalysts.[13] Table II compares the amount of acid extracted into cyclohexane (by the tetraphenylborate anion) with the amount of base extracted into cyclohexane (by two traditional phosphonium catalysts). It is apparent that the tetraphenylborate anion is much more efficient at extracting acid into cyclohexane than traditional catalysts are at extracting hydroxide.

Figure 1 shows that k_{obsd} (s^{-1}) for the hydrolysis of *p*-nitrophenyl acetate is not a linear function of catalyst concentration. Whether this is a result of "saturation" of the catalyst and/or acid in the organic layer, or increased hydration of the ion pair, is not presently known. Similar behavior has been observed for traditional PTC at very high catalyst concentrations.[14]

The hydrolysis of esters and acid halides produces acidic products. Consequently, in a traditional base-mediated PTC reaction, the hydroxide will eventually be neutralized. One must, therefore, replace the hydroxide or begin the reaction with a large excess. In certain acid-mediated PTC reactions, however, the resulting acidic products could serve to increase the rate of the reaction (autocatalysis). Figure 2 illustrates this phenomena for both the catalyzed and uncatalyzed hydrolysis of *p*-toluenesulfonyl chloride in a two-layer aqueous-organic system.[15] The addition of sodium tetraphenylborate greatly increased the rate of hydrolysis while maintaining the autocatalytic nature (Figure 2 insert).[16]

It is likely that there are some mechanistic differences between PTC with a "negatively charged" [10] catalyst and that with a traditional positively charged catalyst. The aforementioned nonlinear relationship of catalyst concentration vs. rate and the extractability of counterions indicate differences. Consider, for example, the hydrolysis of an ester in the organic layer of an acid-catalyzed PTC reaction (Scheme I). The tetraphenylborate anion (Q^-) carries the hydrated proton into the organic layer. The acid-catalyzed reaction occurs (assumed via traditional mechanism). Since protons are not consumed, Q^- gets back the proton at the end of the reaction but looses one molecule of water. Consequently, the ion pair need not return to the aqueous layer, but can continue to catalyze reactions in the organic layer until more water is needed. This is somewhat different from traditional PTC reactions where anions must continually be transferred to the organic layer.

Scheme I



Studies on the use of "negatively charged" [10] phase transfer catalysts in synthesis are currently being completed and will be described in forthcoming publications.[16]

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

References and Notes

(1) M. Makosza and M. Wawrzyniewicz, *Tetrahedron Lett.*, **No. 53**, 4659 (1969).
(2) C. M. Starks, *J. Am. Chem. Soc.*, **93**, 1, 195 (1971).
(3) J. Dockx, *Synthesis*, 441 (1973).
(4) E. V. Dehmlow, *Angew. Chem., Int. Ed. Engl.*, **13**, 170 (1974).
(5) J. H. Fendler and E. J. Fendler, "Catalysis in Micellar and Macromolecular Systems", Academic Press, New York, 1975.
(6) E. V. Dehmlow, *Angew. Chem., Int. Ed. Engl.*, **16**, 493 (1977).
(7) W. P. Weber and G. W. Gokel, "Phase Transfer Catalysis in Organic Synthesis", Springer-Verlag, New York, 1977.
(8) A. W. Herriott and D. Picker, *J. Am. Chem. Soc.*, **97**, 2345 (1975).
(9) M. Mikolajczyk, S. Grzejszczak, A. Zatorski, F. Montanari, and M. Cinquini, *Tetrahedron Lett.*, **No. 43**, 3757 (1975).
(10) The sodium tetraphenylborate catalyst is, of course, a neutral salt. The phrase "negatively charged" refers to the tetraphenylborate anion which is responsible for extracting hydrated protons (via ion-pair formation) into the organic solvent.
(11) In a typical reaction 60 mL of 1.5 N HCl was used as the aqueous layer and 60 mL of cyclohexane containing 0.05 M *p*-nitrophenyl acetate was used as the organic layer. All reactions took place in a thermostated constant temperature bath (25 ± 0.1 °C). In the acid-mediated reactions the appearance of *p*-nitrophenol was monitored spectrophotometrically (865 nm) with time. In the traditional base-mediated reactions, the disappearance of *p*-nitrophenyl acetate was monitored spectrophotometrically (267 nm) with time. Each reaction was repeated at least four times to assure reproducible data.
(12) In addition to sodium tetraphenylborate, an anionic surfactant (sodium dioctylsulfosuccinate, Aerosol-OT), a cation-exchange resin (Dowex 50W-X2, for "triphasic" catalysis), and *p*-toluenesulfonic acid were tested to see if they might also be effective negatively charged phase transfer catalysts. However, even at 60 °C they showed little or no catalytic activity.
(13) E. V. Dehmlow, M. Slopianka, and J. Heider, *Tetrahedron Lett.*, **No. 27**, 2361 (1977).
(14) J. H. Fendler, personal communication on unpublished results.
(15) In both of the autocatalytic experiments (with and without 0.01 M sodium tetraphenylborate) 0.136 M *p*-toluenesulfonyl chloride in 60 mL of cyclohexane was used as the organic layer, and 60 mL of distilled water was used as the aqueous layer. The temperature was 25 °C and the stirring rate was 600 rpm.
(16) Patents pending.

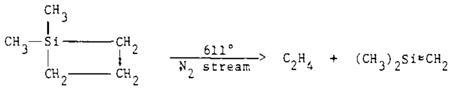
Daniel W. Armstrong,* Mark Godat
Department of Chemistry, Bowdoin College
Brunswick, Maine 04011

Received January 1, 1979

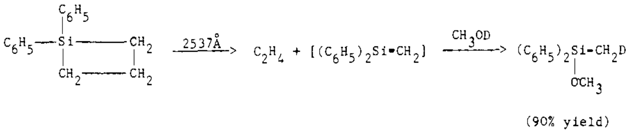
Evidence for Silicon–Carbon and Silicon–Nitrogen Multiple-Bonded (p_π–p_π) Intermediates from Photolysis. Dipolar Character of the Unsaturated Linkages

Sir:

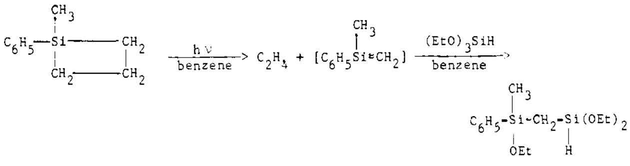
In a previous communication[1] we reported evidence that thermolysis of 1,1-dimethyl-1-silacyclobutane gives an unsaturated intermediate having a highly polarized double bond: $(CH_3)_2Si^{\delta+}\overset{\cdots}{-}CH_2^{\delta-}$. The nature of the evidence was in strong opposition to a diradical formulation for the species being trapped, when *thermolysis* shown below was used for generation. In this regard our evidence and conclusions were in harmony with the pioneering work of Gusel'nikov and Flowers[2a] and with views expressed in a later review article.[2b]



We have previously reported[3] that the *photolysis* of 1,1-diphenyl-1-silacyclobutane yields an unsaturated silicon–carbon intermediate which was trapped with CH_3OD.



However, the nature of the *photochemical* intermediate was really unknown, since a diradical might also give the observed product. To resolve the problem we took under consideration the following well-known and well-documented differences between ≡Si—H and ≡Si—OEt bonds: (1) H^- is a poorer leaving group than EtO^- when silicon undergoes nucleophilic attack;[4] (2) H· is far more easily abstracted from silicon by free-radical attack than ·OEt.[5,6] The higher Si—O bond dissociation energy compared with Si—H is probably responsible for this difference. Based on these considerations the experiments shown were done to clarify the nature of the photochemical intermediate being trapped.[7,8] Product I, from trapping with triethoxysilane, clearly results from addition of EtO to the silicon and $Si(H)(OEt)_2$ to the carbon portion of a highly reactive unsaturated silicon–carbon linkage having considerable dipolar character; nucleophilic or electrophilic attack on an Si—O—C grouping is well known, whereas radical attack under ordinary liquid-phase conditions is unknown for Si—O—C and well known for Si—H. Thus, we are inclined to formulate the photolytic intermediate which is



I (38% glc isolated yield)