Phase-transfer catalysis in reactions of electrophilic aromatic substitution*

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Electrophilic substitution in aromatic compounds under conditions of phase-transfer catalysis is considered. Catalysts of phase transfer of electrophilic reagents are used; their efficiency and the mechanism of their action in organic solvent—water systems are discussed.

Key words: phase-transfer catalysis, catalysts of phase transfer of electrophiles, electrophilic aromatic substitution.

Conducting reactions in two-phase liquid systems (the polar phase of a reagent and the nonpolar phase of a substrate) is a common practice in electrophilic aromatic substitution (nitration, sulfonation, C-alkylation, *etc.*). Quite a number of proposals for using certain additives (normally surfactants) to intensify these processes have been reported in the patent literature, though, as a rule, the effect achieved has not been attributed to phase-transfer catalysis (PTC). Studies dealing with PTC in electrophilic substitution are few in number, compared to those dealing with reactions of nucleophilic reagents (Tables 1 and 2). This provided a reason to consider electrophilic phase transfer catalysis to be an atypical version of PTC. An exhaustive survey of early works (1979—1988) in this field is presented in the monograph by Gol'dberg[1] and in the reviews by Ichikawa *et al.*[8,22] More recent studies, which were not included in these reviews, deal with two new processes carried out under conditions of PTC, *viz.*, chloromethylation and nitrite-initiated nitration (see Table 1), as well as with synthesis of novel catalysts of phase transfer of electrophiles (CPTE), study of their properties, and their testing in the above-mentioned processes. The present paper is devoted to discussion of the most significant aspects of the previous and recent studies.

Phase-transfer catalysts are substances whose addition to a two-phase reaction system increases the rate of the reaction. If one assumes that a reaction occurs in the bulk of the organic phase (this has been proved for almost all of the cases listed in Table 1), one may conclude that the accelerating effect of a catalyst is primarily associated with the transfer of an active form of a reagent, its precursor, and/or electrophilic catalyst from the polar phase into the organic phase. However, the active form of a reagent in electrophilic substitution, E^+, is known to be produced in rapid equilibrium steps involving acid catalysis. When a reaction is carried out in a water—organic solvent two-phase system, a protic acid present in the aqueous phase acts as a catalyst. The catalytic properties of an organic phase in the presence of CPTE depend on the composition of the aqueous phase and the nature and concentration of CPTE, and an analog of one of the known acidity functions can serve as a quantitative measure of these properties. Since phase-transfer catalysts are normally hydrated, it is expedient to use an analog of the Deno—Jaruzelski acidity function, H_R,[23] as a measure of catalytic activity. This function is defined in conformity with protonation equilibrium (1) for trialkylcarbinol as EOH:

$$E^+ + H_2O \rightleftharpoons EOH + H^+ . \qquad (1)$$

Until recently, the "store" of CPTE has been quite small (**1**—**3**) (see Table 2). The first example of purposeful use of electrophilic PTC was azo coupling of *p*-nitrophenyldiazonium chloride with *N*-ethylcarbazole catalyzed by sulfonate **1a** in the CH_2Cl_2—water system[4] (see Table 1). Later, one more effective CPTE, boranate **3**,[2] possessing high lipophilicity and resistance to acids and oxidizing agents, was tested in the same reaction.[19] The catalytic activities of these two CPTE are difficult to compare, since in one of the studies,[2] diazonium tetrafluoroborate, rather than chloride, was used. However, the authors of other papers assert that compound **1a** accelerates the coupling by approximately an order of magnitude with respect to the noncatalyzed reaction,[4] and compound **3** (see Ref. 3) accelerates it by more than three orders of magnitude. A comparison of the rates of azo coupling of diazonium salts with anion **3** in

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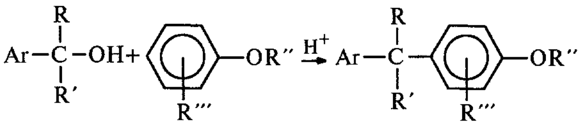
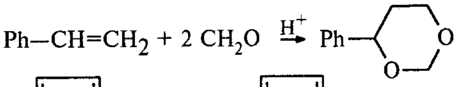
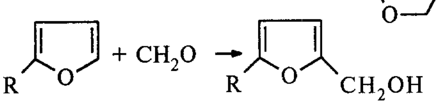
Table 1. Electrophilic phase-transfer catalysis in aromatic substitution

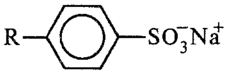
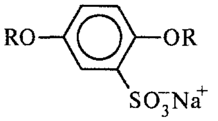
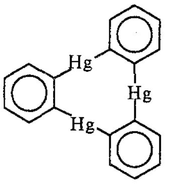
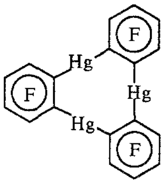
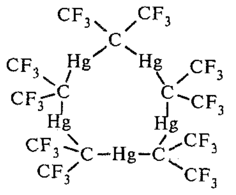
Reaction	System	Catalyst	Reference
$ArN_2X + Ar'H \rightarrow Ar{-}N{=}N{-}Ar'$			
Ar = Ph, n-NO_2—C_6H_4; X = BF_4	Solid phase—C_6H_6; CH_2Cl_2—H_2O	**3**	2,3
Ar = n-NO_2—C_6H_4; X = Cl	CH_2Cl_2—H_2O	**1a**	4
Ar = Ph; X = Br	CH_2Br_2—H_2O	**7**	5
$ArNH_2 + HNO_2 \xrightarrow{H^+} ArN_2^+ \xrightarrow{Ar'H} Ar{-}N{=}N{-}Ar'$			
Ar = n-NO_2—C_6H_4	CH_2Cl_2—H_2O	**3**	6
Ar = C_6F_5, 4-C_5F_5N	CH_2Cl_2—H_2O	**3**	7
$Ph_2NH + HNO_2 \rightarrow Ph_2N{-}NO$	CH_2Cl_2—H_2O	**3**	6
$ArH + HNO_2 \xrightarrow{H^+} ArNO \xrightarrow{[O]} ArNO_2$ Ar = 3-(9-ethylcarbazyl), 1-(2-hydroxynaphthyl)	CH_2Cl_2—H_2O	**3**	6
$R{-}COOR' + H_2O \xrightarrow{H^+} RCOOH + R'OH$			
R = Ph; R′ = Alk, Ar	CH_2Cl_2—H_2O	**3**	8
R = Me; R′ = n-C_6H_4—NO_2	C_6H_6—H_2O	**1a**, **2**	9
 Ar = Ph, n-MeO—C_6H_4; R = Ph, H; R′ = Ph, H, Me; R″ = H, Me; R‴ = m-Me, m-OMe, o-OH	CH_2Cl_2—$(H_2SO_4)_{aq}$	**3**	10
	Organic phase— $(H_2SO_4)_{aq}$	**1**	11
 R = H, Me, CH_2OH	Ⓟ—SO_3H— organic phase—H_2O	**3**	12
$ArH + CH_2O + HCl \rightarrow ArCH_2Cl$	C_6H_6—$(HCl)_{aq}$; $(CHCl_2)_2$—$(HCl)_{aq}$	**4a**, **4b** **5**, **6** *etc.*	13,14
$ArH + HNO_3 \xrightarrow[(NO_2)]{H^+} ArNO_2$	C_6H_6—$(HNO_3)_{aq}$; $(CHCl_2)_2$—$(HNO_3)_{aq}$	**4a**, **4b** **6**, **8**, **9**	15–18

single-phase organic (benzene, dichloromethane) or aqueous media makes it possible to suggest that phase transfer only partially accounts for the acceleration of the reaction and that the acidity of diazonium cation in organic media increases.[3] The first and so far the only example of quantitative characteristization of the acidity of an organic phase during PTC has been given by Ichikawa *et al.*,[22] who studied by spectrophotometry ionization of triphenyl carbinol in dichlorometane contacting with sulfuric acid (a 3.1—59.0 % aqueous solution) in the presence of boranate **3**. In conformity with equilibrium (1) with triphenyl carbinol as EOH, ionization of the latter is expressed by a C_{org} function, similar to H_R:

$$C_{org} = pK_a - \log([R^+]/[ROH])$$

(the $pK_a = -6.63$ value for an aqueous solution of sulfuric acid was used). A comparison of acidity functions of the contacting phases, the organic phase (C_{org}) and the aqueous-acid phase (H_R), indicates that the difference between the acidities of the phases decreases, as the concentration of H_2SO_4 increases, and it almost disappears, when the concentration reaches 60 %. This is probably due to the decrease in the activity of water in a more concentrated polar phase (its logarithm in a 60 % solution of the acid is −0.8). In the presence of dilute H_2SO_4, under the action of CPTE, the organic phase becomes superacidic compared to the aqueous phase. In fact, triphenyl carbinol in dichloromethane, contacting with 25 % H_2SO_4 in the presence of boranate **3**, is ionized by 66 %, *i.e.*, to the same degree to which

Table 2. Catalysts of phase transfer of electrophiles (CPTE)

Compound		Name	Reference
 R = C_{12}—C_{18} *n*-Alk	**(1)** **(1a)**	Alkylbenzenesulfonates R = $C_{12}H_{25}$ — dodecylbenzenesulfonate	4,9,11*
 R = C_{12}—C_{16} *n*-Alk	(2)	1,4-dialkoxybenzenesulfonate	9
$[3,5\text{-}(CF_3)_2C_6H_3]B^-Na^+$	(3)	Sodium tetrakis(3,5-ditrifluoromethylphenyl)boranate	2,3,6—8,10* 12*,19,20
$[C_6F_5]_4B^-M^+$ M = Na, $(Me)_4N$	(4) (4a,b)	Sodium or tetramethylammonium tetraperfluorophenylboranate	19,21 13—15
$R\overset{+}{N}(Me)_2CH_2COO^-$ R = C_{12}—C_{18} *n*-Alk	(5)	*N,N*-dimethyl-*N*-alkylcarboxybetaine	13*,21
$R\overset{+}{N}(Me)_2C_2H_4SO_3^-$ R = C_{12}—C_{18} *n*-Alk	(6)	*N,N*-dimethyl-*N*-alkyltaurobetaine	13—15*,21
	(7)	*o*-Phenylenemercury cyclotrimer	5
	(8)	*o*-Phenylmercury perfluorocyclotrimer	16—18*
	(9)	Perfluoroisopropylidenemercury pentamer	16*

* The references relate only to the use of CPTE, but not to their synthesis or study of their properties.

it is ionized in a 51 % solution of the acid. Thus, CPTE, being a selective transporter, participates in electrophilic catalysis. From this viewpoint, one may speak of electrophilic catalytic activity of CPTE.

The electrophilic catalytic activity of boranate **3** is manifested in phase-transfer alkylation of active aromatic substrates[10] (see Table 1). In this case, an active carbocationic form arises in a preequilibrium, similar to (1). Triphenylmethylation of *m*-dimethoxybenzene in two-phase conditions with **3** as a catalyst occurs even in the presence of a 2.5 % solution of sulfuric acid. Even benzylation by inactive reagents, such as *p*-methoxybenzyl alcohol, occurs with the same CPTE in the presence of 10—22 % H_2SO_4. Sulfonate CPTE, including trifluoromethanesulfonic acid, are absolutely inert in this process.

Apart from compound **3**, a number of other boranates, including perfluorinated boranate **4**, have been synthesized.[19] However, the latter compound was considered to be hygroscopic and unstable and, apparently,

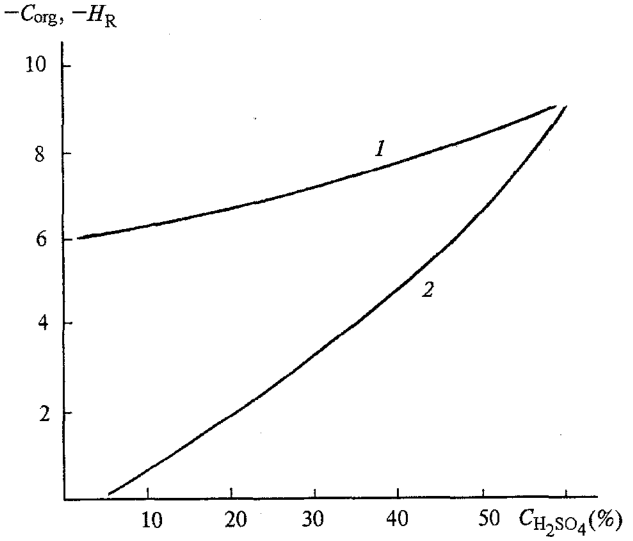


Fig. 1. Comparison of the acidity functions H_R (*2*) and C_{org}[22] (*1*) for aqueous sulfuric acid and an organic phase (CH_2Cl_2) in contact with it.

has not been used as a CPTE. Velichko *et al.*[21] prepared this boranate by a somewhat different procedure (using magnesium synthesis, instead of lithium synthesis). Studies have shown that **4** is extremely acid-resistant, even compared to **3**: no traces of decomposition of this compound in a 55.5 % solution of H_2SO_4 were detected during a month at ambient temperature or during 7 days at 50 °C. Catalyst **4** proved to be resistant to oxidation by atmospheric oxygen or the action of nitrosating reagents.[21] Whereas compound **3** in the CH_2Cl_2—19.7% HNO_3 system containing 2 mol.% $NaNO_2$ (with respect to HNO_3) rapidly decomposes by 70 % over a period of 20 min at 20 °C, compound **4** is quite stable under these conditions.[17]

Nitration of reactive organic compounds (phenols, alkoxybenzenes) by dilute HNO_3 in the presence of nitrites or nitrogen oxides has long been known. However, under conditions of PTC this reaction can be extended to some polycyclic arenes including naphthalene.[15,17,24] Judging by its kinetics, this process is an electrophilic nonbranched chain reaction. The active form assumed for the reaction is protonated nitrogen dioxide, which attacks an aromatic substrate with the recovery of nitrous acid, which continues the chain:

$$HNO_3 + HNO_2 \rightleftharpoons N_2O_4 + H_2O$$

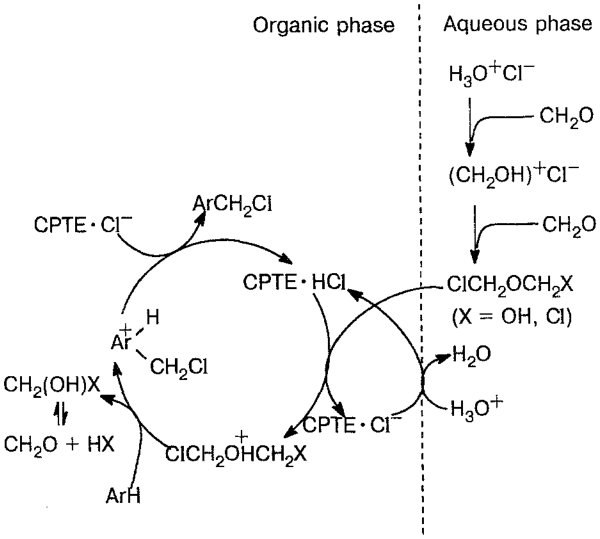
$$N_2O_4 + H^+ \rightleftharpoons (N_2O_4H)^+$$

$$ArH + (N_2O_4H)^+ \longrightarrow ArNO_2 + HNO_2 + H^+$$

This mechanism has been confirmed by mathematical simulation of the kinetics of nitration of acenaphthene.[17]

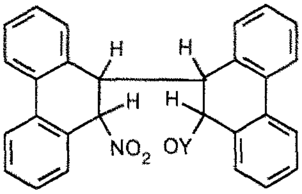
The efficiencies of sulfobetaine (**5**, R = stearyl) and boranate (**4b**) as CPTE in nitration are quite different: the activity of the former is low, accelerating the reaction by only a factor of two, while the latter accelerates it by a factor of almost 300. Replacement of the tetramethylammonium cation by Na^+ results in an additional 25-fold acceleration, and the overall catalytic effect of **4a** is almost four orders of magnitude. In view of the fact that the formation of an active form is acid-catalyzed, it is very likely that the nature of the cation in **4** has a substantial effect on its ability to increase the acidity of the organic phase. In the case of phase-transfer-catalyzed chloromethylation,[13,14] increase in the acidity of the organic phase through the action of CPTE does not necessarily result in an increase in the yield of a target product (see Table 1). The reaction was carried out in a system consisting of benzene (or 1,2-dichloroethane) and a solution of paraform in 35 % HNO_3 at 50 °C in the presence of various CPTE, *viz.*, **4**, **5**, **6**, *etc.* It was found that the reaction occurs in the bulk of the organic phase, and lipophilic dichlorodimethyl and/or chloroxydimethyl ethers are precursors of the active form. In this case, the function of CPTE is also to increase the acidity of the organic phase, which is necessary for generation of the active form of the electrophilic reagent (Scheme 1).

Scheme 1



The rate of the reaction increases in the presence of any of the above-listed CPTE. In the absence of these, the reaction proceeds as a self-catalyzed process, which hampers a quantitative evaluation of the effectiveness of the catalysts. The reaction is also accelerated in the presence of dimethylethylstearylammonium chloride, which probably transfers hydrochloric acid to the organic phase. However, compound **4a**, which ensures the maximum rate of the reaction,[13] leads to very low yields of target product, and at high concentrations of CPTE, a polymer is produced, instead of target product. The most effective CPTE in terms of both the reaction rate and the yield of a chloromethyl derivative are compounds **6** and **4b** (see Ref. 13). Chloromethyl derivatives of active aromatic substrates are prone to self-condensation in the presence of acidic catalysts. This means that the optimal yield of these compounds can be achieved at a specified controlled acidity of the organic phase, which is ensured by **6** or **4b**.

In the nitrite-initiated nitration of phenanthrene[24] under conditions of PTC with **4a** as the catalyst, only some of the converted substrate affords normal mononitro compounds, while two thirds of it yields dimers: a mixture of 9,10,9′,10′-tetrahydro-10-nitro-9,9′-biphenanthryl-10-ol (**10a**) and its nitrate (**10b**).



10a: Y = H
10b: Y = NO$_2$

Of considerable interest are CPTE of a new type, *viz.*, macrocyclic organometallic compounds **7**, **8**, and **9**. The crown-like molecules of these compounds, which are rather lipophilic, unlike the widely known crown ethers, exhibit affinity to anions and not to cations. The corresponding complex anions can serve as effective transferring reagents that transport active electrophilic species from the aqueous phase into the organic phase.

Normal crown ethers solubilize cations in the organic phase.[1] Macrocyclic molecules **8** and **9**, which strongly bind an anion, substantially increase the electrophilicity of a reagent (or activity of the proton) in a nonpolar organic phase, contacting with an aqueous phase that usually contains a mineral acid and a reagent. When such a CPTE is added to the system, the effect can be visually observed: the colorless organic phase containing indicator quantities of triphenyl carbinol and existing in an equilibrium with a dilute mineral acid changes to an intense yellow color owing to the appearing carbocation (Scheme 2).

Scheme 2

$$\text{CPTE} + X^-H^+ \rightleftharpoons (\text{CPTE X})^-H^+ \ \text{(aqueous phase)}$$
$$Ph_3COH + (\text{CPTE X})^-H^+ \rightleftharpoons$$
$$\rightleftharpoons Ph_3C^+X^- + H_2O + \text{CPTE (organic phase)}$$

As was discussed above, high acidity of the organic phase is caused by the transfer of protons into it and by low concentration of water molecules in this phase.

At this time, there have been only two examples of using catalysts of the type under consideration in PTC (see Table 1). The first of these was the use of *o*-phenylmercury cyclotrimer **7**, which had a weak but quite noticeable catalytic effect in azo coupling of phenyldiazonium with 2-naphthol.[5] The use of compound **7** as a CPTE in typical electrophilic substitution reactions is hampered by its low stability toward acids, which is characteristic of normal organomercury compounds. The resistance to acids of perfluorinated macrocyclic organomercury compounds, for example, **8**, is appreciably higher. In fact, the latter is stable in a 21 % solution of HNO$_3$ at 20 °C for several hours.[18]

A significant characteristic feature of mercury-containing macrocyclic compounds **8** and **9** is their ability to form complexes with halide anions; these complexes exist in solutions or even can be isolated.[5,25,26] The role of the nature of the anion present in the acid medium for the effectiveness of these CPTE can be demonstrated using nitrite-initiated nitration of acenaphthene in the benzene—21.3 % nitric acid system as an example.[16,18] In the absence of halide ions, perfluoro-*o*-phenylmercury cyclotrimer **8** (like a halide ion itself) exhibits no catalytic properties, and the yield of nitro compounds does not exceed 1 %. In the presence of NaCl (0.13 moles per mole of HNO$_3$), the addition of the cyclotrimer accelerates the reaction by more than three orders of magnitude, and the reaction is completed over a period of less than 1 h. Thus, chloride anion acts as a promoter of the catalytic phase-transfer nitration.

Perfluorinated isopropylidenemercury cyclopentamer **9** exhibits a catalytic effect also in the absence of halide ions, but when halide ions are added, this effect is much enhanced: the reaction rate increases by three orders of magnitude compared to that of the noncatalyzed reaction.[27] This CPTE, unlike compound **8**, effectively transfers proton not only from solutions of hydrochloric acid, but also from solutions of HNO$_3$ or H$_2$SO$_4$ (see Scheme 1, X = NO$_3$, HSO$_4$).

A number of interesting peculiarities of these reactions still need to be explained. These are: the existence of an induction period when **8** is used, in contrast to **9**; the disappearance of this period when nitro compounds are added to the system; and dissimilar characters of the accelerating action of added nitrobenzene and nitroacenaphthene. It has been found that the effects observed refer only to catalyzed reactions, while rate constants of noncatalyzed reactions remain constant under these conditions. It should also be noted that the solubilities of **8** and **9** in benzene are rather low ($1 \cdot 10^{-4}$ and $5 \cdot 10^{-6}$ mol L^{-1}, respectively), and these quantities of CPTE are ineffective.[16] Therefore, quantities of **8** and **9** 1—2 orders of magnitude greater than those that could pass into solution were used. Thus, in the absence of substantial amounts of nitro compounds, which increase the solubility of the catalysts, the reaction system acted as a three-phase system.

The data accumulated until the present time allow one to argue that phase-transfer catalysis of electrophilic aromatic substitution provides the same possibilities and advantages as conventional PTC.

An obvious advantage of PTC is the possibility of performing heterogeneous processes under conditions where phase transfer no longer limits the reaction rate. In addition, there appears a possibility of studying kinetics and mechanisms of reactions without using complicated procedures of dealing with highly dilute solutions of a nonpolar substrate in a polar phase.[13,17]

It was mentioned above that CPTE possess intrinsic catalytic activities in acid-catalyzed electrophilic substitution in two-phase systems, which makes it possible in some cases to do away with using large excesses of concentrated acids. For example, mononitro derivatives of some polycyclic arenes can be obtained in high yields by using a small excess of dilute (14—30 %) nitric acid.[15,24]

The significance of methods of PTC is especially ponderable in those cases where there is no alternative. Perfluorinated aryldiazonium salts are known to be stable only in concentrated solutions of acids, while in dilute solutions, nucleophilic substitution of hydroxyl for fluorine readily occurs. Diazotization carried out under phase transfer conditions and subsequent azo coupling of the perfluorinated diazonium salts isolated *in situ* make it possible to prepare azo compounds with inactive azo components.[17] Chloromethylation of active ($\sigma_{\mathrm{Ar}^+} \le -0.5$) aromatic substrates,[13,14,28] which cannot be accomplished in homogeneous acidic media, because of self-condensation of primary reaction products, is another example. Hydroxymethylation of furan, sylvan, and furfuryl alcohol in acidic sulfocationite—organic phase—aqueous solution of formaldehyde three-phase systems is of interest in the same respect.[12] In these processes, the target hydroxymethyl derivatives were obtained in high yields. Carbonyl compounds are known to react with active aromatic compounds under conditions of acid catalysis to give di- or triarylmethane derivatives, rather than carbinols, since the first step of the reaction, the formation of carbinols, occurs much more slowly than arylmethylation of the substrate by carbinol.[29]

Thus, one may conclude that no universal CPTE, which would be equally appropriate in any case, exists. One might expect that the range of reactions carried out under conditions of electrophilic PTC would be extended in the near future. Therefore, the selection of effective and available CPTE would be a key problem for industry. At present, only alkylbenzenesulfonates and, to some extent, carboxy- and sulfobetaines (like **5** and **6**) are easily available and low-cost. However, these compounds cannot substantially increase the acidity of the organic phase. Hence, in those cases where increase in the acidity is necessary, there is yet no alternative to boranates (**3** and **4**), which are rather difficult to obtain. Therefore, the search for catalysts of a new generation having crown-like macrocyclic structures and possessing an affinity for anions attracts considerable interest.

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