could add HBr ionically to form product directly. The inability to gain evidence for alkenes again argues against this mechanism. In addition separate isotopic labeling studies by Tanner[10b] and Ronneau, *et al.*,[20] have failed to provide evidence for "free" alkene intermediates in brominations of 1-bromobutane. 1,2-Bromine atom migrations in free radicals have been previously reported[5-8] usually when a more stable radical is being produced. Traynham,[8] however, has reported products corresponding to a 1,2-bromine migration from a primary to a tertiary carbon.

The failure to note 2-bromobutane from the Br_2 bromination reactions may be due to the decreased rate of chain transfer of $BrCCl_3$ relative to Br_2, but the observation of 10% radiolabeled bromine in the 2 position of 1,2-dibromobutane produced when ^{82}Br 1-bromobutane is brominated with isotopically normal Br_2 suggests that a similar migration is operative in this system.

The observation of the 2-bromobutane product, which must result from β-hydrogen abstraction, is indicative that the ratio of β to γ hydrogen abstraction may be higher than the value obtained from the relative yields of the dibromination products.

The formation of small amounts of *meso*- and *dl*-2-3-dibromobutane is also explicable on the basis of the rearrangement product. A bromotrichloromethane bromination of 2-bromobutane produced these compounds in the same ratio observed in the 1-bromobutane system (~50:50).

Another major difference in the two modes of bromination is the absence of 1,1-dibromobutane formation in the $BrCCl_3$ system while it is a significant product from the Br_2 reaction. This may be due to an unfavorable dipole–dipole interaction between the chlorines of the near-planar $CCl_3\cdot$[21] and the substrate bromine in the transition state for α-hydrogen abstraction.

Experimental Section

With the exception of 1,1-dibromobutane, all chemicals were commercial products. 1,1-Dibromobutane was synthesized by the method of Conly[11] and identified on the basis of its nmr spectrum (CCl_4), δ 0.98 (distorted t, 3), 1.51 (m, 2), 2.40 (m, 2), 5.75 (t, 1). Purification of 1-bromobutane was accomplished by the method of Tanner.[10] All other materials were used without further purification.

Photolyses.—Small portions of approximately 8.5:1 molar ratios of 1-bromobutane to bromotrichloromethane with chlorobenzene added as internal standard were placed in Vycor tubes, degassed by three freeze–thaw cycles, and sealed under vacuum. These tubes were placed in a larger Vycor tube and an ethylene glycol–water mixture from a thermostated bath was pumped through to regulate the reaction temperature.

Photolyses were conducted for various lengths of time with a 275-W G. E. sun lamp. Products were quantitatively determined with a 12 ft × 0.25 in. 20% SE-30 on Chromosorb W glpc column (80° column temperature with 30 ml/min carrier gas flow). The detector response was calibrated using known mixtures. Results are tabulated in Table I.

Titration Experiment.—Solutions containing 2.00 ml of reaction mixture were photolyzed at 20°. The tubes were opened and a 10.0-μl sample was analyzed by glpc. The remaining solution was immediately washed into a flask with a water–isopropyl alcohol mixture and titrated with 0.001 *M* NaOH to a phenolphthalein end point.

Registry No.—1-Bromobutane, 109-65-9; bromotrichloromethane, 75-62-7; 2-bromobutane, 78-76-2.

Acknowledgment.—We thank the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

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(20) C. Ronneau, J. P. Soumillion, P. Dejaifve, and A. Bruylants, *Tetrahedron Lett.*, 317 (1972).

(21) C. Hesse and N. Leray, *Mol. Phys.*, **22**, 137 (1971).

Anomalous Hydrogen Exchange Reactions in HSO_3F–SbF_5

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Olefins, when added to SbF_5–HSO_3F solutions in the presence of alkylcycloalkanes or alkanes, are converted into the corresponding paraffin. However, labeling studies using tritiated acid and methylcyclohexane-d_{14} show that significant amounts of product do not arise *via* a normal carbonium ion path, which would have introduced one proton from the acid and one from the hydride donor into the products. Instead, much of the product appears to form by a process in which the alkylcycloalkane transfers two hydrogen atoms to the olefin. The possibility of a chain reaction at the acid–hydrocarbon interface or the intervention of radical cations leading to these results is considered.

Solutions of antimony pentafluoride in fluorosulfonic acid and other solvents are commonly used for the study of carbonium ions. Much of this work is due to enthusiasm with which Olah and coworkers have explored the field.[1] Recently, a study has been done of the behavior of alkyl cations in the SbF_5–tritiated HSO_3F system wherein the ions were formed by solvolysis of halides and trapped by hydride transfer to yield kinetically controlled products.[2] There it was shown that during many rearrangements a species which contained a very loosely bound and hence exchangeable proton formed. The species could be considered as a protonated alkylcyclopropane inter-

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(1) (a) G. A. Olah, Abstracts of the 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1962, p 45; (b) G. A. Olah, W. S. Tolgyesi, J. S. McIntyre, I. J. Bastion, M. W. Meyer and E. B. Baker, Abstract A, 19th International Congress of Pure and Applied Chemistry, London, June 1963, p 121; (c) G. A. Olah and J. A. Olah, "Carbonium Ions," Vol. II, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N. Y., 1970, p 715.

(2) G. M. Kramer, *J. Amer. Chem. Soc.*, **92**, 4344 (1970).

mediate or transition state in the rearrangement process.

To provide another source of information concerning cation nature and behavior, olefin protonation has been investigated in the same media. Olah has indicated that alkyl cations can be formed from olefins in SbF_5–HSO_3F, but notes that the nmr resonance spectra are worse than obtained from solvolytic routes to the ion for obscure reasons.[1c] Thus it was expected that, although polymerization would be a competing reaction, simple olefins could be protonated once by the acid forming a cation which could be trapped by hydride transfer from a good donor like methylcyclopentane.

If the reaction was carried out in the same SbF_5–tritiated acid used in the alkyl halide solvolysis studies, one would expect the following normal sequence of reactions

$$C_nH_{2n} + L^+ \longrightarrow C_nH_{2n}L^+ \qquad (1)$$

$$C_nH_{2n}L^+ + CH_3\text{-}c\text{-}C_5H_9 \longrightarrow C_nH_{2n+1}L + CH_3\text{-}c\text{-}C_5H_8^+ \qquad (2)$$

In eq 1, L^+ is a proton with the average specific activity of the acid. These reactions lead to the formation of a paraffin, $C_nH_{2n+1}L$, which has acquired one hydrogen from the acid and one from methylcyclopentane. Accordingly, the specific activity of the paraffin produced is expected to reflect the introduction of one proton from the acid. However, when the experiments were performed, it was found that many olefins were converted into paraffins in reasonable yields but with substantially less than one proton having been derived from the acid. These anomalous results are reported in the paper, and speculation is presented regarding the mechanism and possible intervention of radical cations in the reactions.

Experimental Section

Tritium Exchange.—Olefins were mixed with a large excess of a hydride donor like methylcyclopentane (1:50), and the solution was then contacted with 2 *M* solutions of SbF_5 in HSO_3F. The acid had a specific activity of *ca.* 1 mCi/ml and had been diluted with about 5% H_2O to catalyze proton exchange between cations or intermediates present during rearrangements and the acid system.[2] A hydrocarbon–acid volume ratio of 0.5 was used in nearly all experiments.

Experiments were run at −50°, either in nmr tubes or in a modified Kjeldahl flask fitted with a mechanical stirrer and an injection port. The reagents were vigorously mixed for 10 sec and then allowed to settle. The hydrocarbons separated immediately from the acid and were quickly removed by vacuum distillation at −50° and condensed in a −80° trap. They were analyzed in a radioassaying gas chromatograph system. The extent of exchange in the products was determined by comparing the specific activity of each component with that of a standard solution of methylcyclopentane which had equilibrated 11 protons in the same acid system (2).

Deuterium Exchange.—Methylcyclohexane-d_{14} (Norell Chemical Co.) was employed instead of methylcyclopentane in a similar series of experiments to those described above. In this case however, the acid did not contain any tritium. After vacuum distillation the products were separated on a gas chromatograph from which the paraffin corresponding to the reacting olefin was trapped in a gas collection vessel. This gas was analyzed by mass spectrometry on a CEC-21-103C spectrometer to determine the extent of deuterium exchange (50-μA trap current and 70-eV electrons).

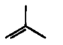
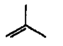
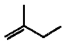
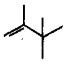
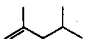
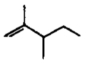
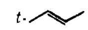
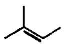
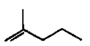
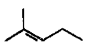
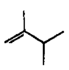
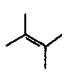
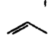
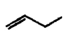
Results and Discussion

The SbF_5–HSO_3F system is known to provide one of the strongest acids available. As a consequence, alkyl cations formed *via* solvolysis appear to be relatively stable and hence can be observed by nmr spectroscopy. Thus, even the addition of 5% water does not provide enough nucleophiles to induce sufficient proton exchange to prohibit the apparent observation of a *tert*-butyl or *tert*-amyl cation at −50°.

Accordingly, it is reasonable to expect that the addition of isobutylene to such an acid should result in instant protonation of much of the olefin forming a *tert*-butyl ion which should either take up a quiescent residence in its nonnucleophilic surroundings or perhaps add to another incoming butylene and ultimately form a polymer of variable size. If the acid contained tracer concentrations of tritium, the *tert*-butyl ion would be expected to have acquired a proton with the same specific activity as in the acid unless protonation were slow and a kinetic isotope effect was important. In that case substantially less tritium would find its way into the butyl ion than was in the acid. After subsequently being trapped by hydride transfer from methycyclopentane, the isobutane formed would then appear to have less radioactivity than would be expected from the acquisition of a proton from the acid.

In Table I are shown the apparent number of exchanged protons present in paraffins obtained by reacting a series of olefins with methylcyclopentane or methylcyclohexane in 2 *M* SbF_5–$H(T)SO_3F$ at −50°. While there is some scatter in the data it is clear that propylene, isobutylene, 2-methyl-1-butene, and 2,3,3-trimethylbutene were converted into paraffins in fairly good yields with low tritium contents.

TABLE I
OLEFIN PROTONATION BY 2 *M* SbF_5–$H(T)SO_3F$ APPEARS LOW, −50° [a]

Olefin	Hydride donor[b]	Reactor[c]	RH, %[d]	No. of H_{ex}
	MCP	K	32	0.1
	MCH	K	27	0.5
	MCP	K	30	0.5
	MCH	K	100	0.5
	MCH	K	78	0.9
	MCP	K	40	1.8
	MCP	K	100	0.2
	MCP	K	100	2.7
	MCP	N	44	0.9
	MCP	N	40	0.6
	MCP	N	12	0.9
	MCP	N	31	0.9
	MCP	N	49	0.8
	MCP	N	30	0.4
	MCP	N	97	2.9

[a] Donor/olefin ratio 50:1. [b] MCP, methylcyclopentane; MCH, methylcyclohexane. [c] K, modified Kjeldahl flask; N, nmr tube. [d] The paraffin with the same C skeleton as the olefin.

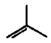
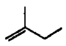
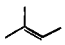
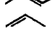
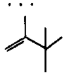
To explain the unusually low tritium results the following possibilities have been considered. (1) There was a rate-limiting protonation with a strong isotope effect. (2) There was a rapid chain reaction at the acid–hydrocarbon interface after the acid had protonated an olefin resulting in first hydride transfer from the donor to the cation and then proton transfer from the new cation to another olefin. (3) Methylcyclopentane or methylcyclohexane extensively exchanged protons with the acid thus reducing the latter's specific activity before the acid protonated the olefin. (4) A new type of reaction involving the oxidation of either the olefin or the cycloalkane to a radical cation followed by an H_2 or an H_2^- transfer has occurred.

The low values are not likely to have been caused by an isotope effect in a slow protonation step for several reasons. First, if such an effect was really in operation at −50°, it should have been much more pronounced. Thus one can estimate that a normal effect at this temperature would have resulted in the acquisition of only 0.02 exchanged protons.[3] This is much less than was observed, and the isotope effect is inconsistent with the data in Table I.

A second and stronger reason for disregarding the isotope effect explanation is obtained however by considering the results of reacting isobutylene and other olefins with methylcyclohexane-d_{14} under similar conditions but with unlabeled acid (Table II). There it is seen that the paraffinic product has been produced after multiple exchange with methylcyclohexane. This result is clearly inconsistent with a rate-limiting protonation of the olefin which would be necessary for the isotope effect to be responsible for the data.

TABLE II

DEUTERIUM TRANSFER FROM MCH-d_{14} TO OLEFINS IN 2 *M* SbF_5-HSO_3F[a]

Olefin	Reactor	T, °C	D distribution in paraffin d_0	d_1	d_2	d_3	d_4	d_5
	K	−50	+	89	11			
	K	−20	+	65	35	+	+	
	K	−50	−	70	20	10	+	
. . .[b]	N	−50	?	61	16	16	7	
	K	−50	0	77	23	+		
	K	−50	0	80	20	+	+	+
	K	−50	0	60	40			
. . .[b]	N	−50	0	50	50			
	K	−50	8	71	13	4.5	2.4	1.3

[a] MCH-d_{14}/olefin ratio 50 : 1. [b] These experiments used anhydrous HSO_3F. The other reactions were run with 5% H_2O present.

The possibility of a rapid chain reaction at the acid–hydrocarbon interface is difficult to assess. For it to be responsible for the observations would require that the adsorption of the olefins into SbF_5-HSO_3F was slow relative to the acquisition of a proton from a methylcyclopentyl cation, at the interface or in the hydrocarbon phase. If this condition actually obtains, the anomalous hydrogen exchange results are readily explained.

The existence of such an interfacial chain reaction, although not subject to quantitative evaluation at this time because of lack of information of both salient events (the rate of absorption and the rate of proton transfer from the methylcyclopentyl cation), is considered to be doubtful for several reasons.

One reason is that reactions were carried out in the two types of reactors: nmr tubes and a modified Kjeldahl flask. Both reactors were well mixed, the Kjeldahl reactor certainly more effectively and yet anomalous results were obtained in each. As efficient mixing should have led to more rapid adsorption of olefin in the acid, one might have expected a trend to less anomalous data in the Kjeldahl experiments, but it is not apparent.

Another reason for questioning a surface chain reaction is the high yield of propane when propylene reacted with either methylcyclopentane or methylcyclohexane-d_{14}. In these reactions the chain-carrying proton transfer

$$C_3H_6 + CH_3\text{-}c\text{-}C_5H_8^+ \longrightarrow i\text{-}C_3H_7^+ + CH_3\text{-}c\text{-}C_5H_7$$

from the cyclic cation to propylene is substantially endothermic (~10–15 kcal/mol) and hence unlikely to occur in the hydrocarbon phase. Nevertheless, such a possibility exists and is an alternate to the reaction to be proposed below.

The possibility of methylcyclopentane diluting the specific activity of the acid by rapid exchange prior to protonation of the olefin can be discounted for several reasons.

(a) The specific activity of recovered methylcyclopentane always showed that less than one proton had been exchanged with the acid and the exchange of one would only have diluted the activity by 12%. (b) Nmr investigations of 2 *M* SbF_5-HSO_3F solutions (with 5% H_2O) that were mixed with methylcyclopentane at and above the temperature of the tracer experiments showed neither methylcyclopentane nor the methylcyclopentyl ion in the acid. (c) Tertiary ions like $t\text{-}C_4H_9^+$ and $t\text{-}C_5H_{11}^+$ are trapped by hydride transfer much faster than they exchange protons *via* olefin formation in this acid.[2]

An oxidation reaction which would be compatible with our results has been observed in the mass spectrometer[4] and in vapor phase radiolysis studies by Ausloos and his coworkers.[5,6] They have formulated H_2 and H_2^- transfer reactions as illustrated in eq 3 and 4. The latter possibility provides a rational

$$C_nH_{2n} + c\text{-}C_6H_{12}^+ \longrightarrow C_nH_{2n+2} + C_6H_{10}^+ \quad (3)$$

$$C_nH_{2n}^+ + c\text{-}C_6H_{12} \longrightarrow C_nH_{2n+2} + C_6H_{10}^+ \quad (4)$$

explanation of the exchange data and is a major alternate to the proposal of an interfacial chain reaction.

In the remainder of this paper we will discuss the data in terms of the hypothetical existence of radical cations. Before doing so, however, we must report two pieces of negative information which indicate that *stable*, long-lived radicals or radical cations are not present. First, attempts have been made to detect stable radicals in the acid by esr at −50°, but they

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[3] An estimation was made by extrapolating the hydrogen isotope effect data in L. Melander, "Isotope Effects on Reaction Rates," Ronald Preske, New York, N. Y., 1960, p 22. Use is made of eq 2–10 assuming a stretching frequency of *ca.* 3000 cm^{-1}.

[4] M. S. B. Munson, J. L. Franklin, and F. H. Field, *J. Phys. Chem.*, **68**, 3098 (1964).

[5] P. Ausloos and Sharon G. Lias, *J. Chem. Phys.*, **43**, 127 (1965).

[6] R. D. Doepker and P. Ausloos, *ibid.*, **44**, 1951 (1966).

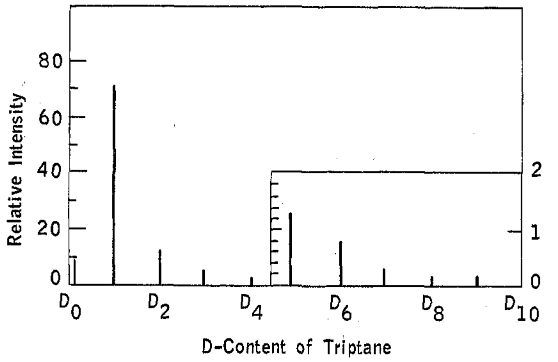


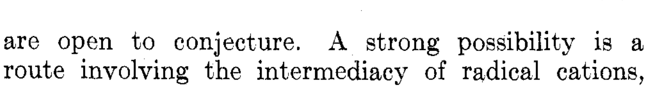
Figure 1.—MCH-d_{14} + trimethylbutene undergo extensive exchange.

have thus far been unsuccessful. Second, experiments have been run which were designed to detect these species by chemically induced dynamic nuclear polarization (CIDNP) by carrying out the reactions in an A-60 nmr spectrometer, but they have also been unsuccessful. Neither of these results however is considered to be conclusive evidence against the possible presence of short-lived radical cation intermediates. Since they do present a viable alternative to the proposal of the interfacial chain reaction and their formation would be consistent with the oxidizing ability of either SbF_5 or HSO_3F, the following analysis of the exchange data is appropriate.

The data in Table II indicate that the isobutane which formed contained significant amounts of $C_4H_8D_2$ and $C_4H_7D_3$ as well as more highly deuterated derivatives besides the normal expected product C_4H_9D. The multiple deuterium incorporation could not have arisen by transfer of deuterium from methylcyclohexane to the acid and then to the butyl fragment because this would be inconsistent with all the tritium results and the nmr spectral observations which show that the alkyl ion is not engaged in rapid exchange with acid protons.

The implication of the observation of multiple deuterium transfer is that a rather direct exchange process between methylcyclohexane and isobutylene occurred which did not involve the passage of protons from one reagent to the acid and then to the other. Clearly to the extent that the same reaction occurred in the tritium experiments, isobutylene would have been converted into isobutane without any tritium incorporation.

The results of the tritium and deuterium experiments taken together imply that isobutylene is converted into isobutane by more than one path. One is the normal carbonium ion route, A; the other or others



$$i\text{-}C_4H_8 \xrightarrow{SbF_5\text{–}HSO_3F} \xrightarrow{A} t\text{-}C_4H_9{}^+ \xrightarrow{MCP} i\text{-}C_4H_{10} \qquad (A)$$

$$\xrightarrow{-e} [i\text{-}C_4H_8{}^+] \xrightarrow{MCP} i\text{-}C_4H_{10} + R^+ \qquad (B)$$

are open to conjecture. A strong possibility is a route involving the intermediacy of radical cations, B. The SbF_5–HSO_3F system provides an oxidizing atmosphere and might abstract an electron either from the cycloalkane or the olefin. If this happened, the H_2 or $H_2{}^-$ transfer illustrated in eq 3 and 4 could naturally occur, just as in the gas phase.

Many questions about H_2 transfer reactions in the gas phase are unanswered at this time. Thus, whether the transfer represents a concerted or stepwise reaction or if electron transfer between the reactants leads to an immediate equilibrium between the olefin, cycloalkane, and radical cation of each, eq 5, is not

$$C_nH_{2n} + c\text{-}C_6H_{12}{}^+ \rightleftharpoons C_nH_{2n}{}^+ + c\text{-}C_6H_{12} \qquad (5)$$

known. On the other hand, much is known about the reactions which appears related to those of this study. Thus Doepker and Ausloos[5] have shown that the $H_2{}^-$ transfer is a general reaction observed with many paraffins and cycloparaffins in addition to methylcyclopentane and methylcyclohexane.

In Table III the results of trapping propylene with methylcyclopentane, isobutane, n-pentane, and cyclopentane in the tritiated acid system are shown. They are compared with the relative efficiency of the compounds to transfer $H_2{}^-$ in the vapor phase to $C_3D_6{}^+$. The tracer results indicate that the H_2 transfer reaction is a general phenomenon in solution, but a quantitative relationship between the two sets of data is clearly lacking and a further kinetic analysis is not warranted at this time.

TABLE III

TRAPPING PROPYLENE IN SbF_5–$H(T)SO_3F^a$

	Propane, %	No. of H_{ex}	$k_{H_2}{}^b$
Methylcyclopentane	100	0.2	0.89
Isobutane	20	0.1	0.23
n-Pentane	17	0.2	1.12
Cyclopentane	2	0.4	0.95

[a] −50°; RH/C_3H_6 ratio 50:1. [b] C_5D_{10} was the reference compound, ref 5.

Returning to Table I it may be noted that the low-molecular-weight α olefins, propylene, 2-methyl-1-propene, 2-methyl-1-butene, 2-methyl-1-pentene, and 2,3-3-trimethylbutene, generally gave evidence of the radical cation route. On the other hand, all the linear butenes and some of the internal olefins acquired one or more protons from the acid and hence gave no indication of any unusual chemistry. The deuterium results of Table II, however, indicate that both the internal olefin, 2-methyl-2-butene, and its isomer, 2-methyl-1-butene, behave in a very similar manner. In both cases about 20% $C_5H_{10}D_2$ and 80% $C_5H_{11}D$ were formed with small amounts of more highly deuterated pentane. The extent of $H_2{}^-$ transfer from methylcyclohexane is less than from methylcyclopentane in the radiolysis experiments, $k_{MCH} = 0.55$ *vs.* $k_{MCP} = 0.89$, so that the deuterium experiment is fairly consistent with the tritium exchange data.

Similarly, about 20% of the propane formed from propylene in the tritium experiments could be attributed to the carbonium ion route while 80% could be due to a radical cation path. This is consistent with the deuterium experiment where 40–50% of the propane was $C_3H_6D_2$.

2,3,3-Trimethylbutene was quantitatively converted into triptane when reacted with methylcyclohexane in the tritiated acid, about 45% being formed *via* the carbonium ion. In the deuterium experiment somewhat more of the normal product was obtained but of greater interest was the fact that significant quantities of d_2, d_3, . . ., d_9 trimethylbutanes were found. Such extensive exchange was also obtained with isobutylene and the methylbutenes and suggests that after a D_2^- transfer occurs in solution the products are able to react several more times before separating. Thus the reactants and product participating in the radical cation exchange appear to undergo reaction while in a solvent cage.

In the trimethylbutene experiment some triptane-d_0 was also formed. This was probably formed by allylic hydride transfer from triptene to the triptyl ion. The relative intensity of the d_0 through d_9 isomers is shown in Figure 1.

Assuming that the reactions observed involve radical cations, it is likely that they are examples of eq 4 and hence an H_2 transfer. This may be inferred from the ionization potential or appearance potential of the respective radical cations. In Table IV it may be seen that saturated compounds generally are more difficult to oxidize than olefins although the difference between propylene and methylcyclopentane or methylcyclohexane is not large. This question ought to be the subject of future research.

In summary, a dual approach to the reaction of olefins in the SbF_5–HSO_3F system has shown that in addition to normal carbonium formation and reactivity much of the olefin reacts *via* an unexpected route. Several possible routes exist. One involves an interfacial chain reaction in which the olefin is protonated and extracts a hydride from the donor forming a cation which then protonates another olefin, etc. An alternative involves the formation of radical cationic intermediates. In any event, the addition of olefins like propylene or isobutylene to SbF_5–HSO_3F solutions in the presence of hydride donor does not proceed to paraffin products exclusively by a normal path where one proton is transferred by the acid and the other from the hydride donor.

TABLE IV
APPEARANCE POTENTIALS OF REPRESENTATIVE RADICAL CATIONS

Ion	AP or IP, eV[a]
$C_3H_6^+$	9.74
i-$C_4H_8^+$	9.23
$(CH_3)_2C{=}CHCH_3^+$	8.8
CH_3-c-$C_6H_{11}^+$	9.9
CH_3-c-$C_5H_9^+$	9.9
i-$C_4H_{10}^+$	10.57

[a] J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, NSRDS-NBS (26), June 1969.

Registry No.—Antimony pentafluoride, 7783-70-2; fluorosulfonic acid, 7789-21-1.

Stable Carbocations. CXXXIV.[1] Protonation of Mono- and Dihydroxybenzenes and Their Methyl Ethers in Superacids

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The protonation of mono- and dihydroxybenzenes and their methyl ethers was studied in four different superacid media, HF–SbF_5 (1:1 M:M)–SO_2ClF (I), HSO_3F–SbF_5 (1:1 M:M)–SO_2ClF (II), HSO_3F–SbF_5 (4:1 M:M)–SO_2ClF (III), and HSO_3F–SO_2ClF (IV) by low-temperature nmr spectroscopy. The sites of protonation (O- *vs.* C-) were dependent upon the acid media used. The structures of the formed ions were assigned based on their nmr (^1H and ^{13}C) spectra. Isomeric ions derived from the same precursor were also observed. Stability of hydroxy(alkoxy)benzenium ions, including isomeric ion forms derived from the same precursors and the relative ease of protonation is discussed in terms of steric, resonance, and inductive effects. Phenyloxonium ion (O-protonated phenol) formation was generally observed in HF containing small amounts of antimony pentafluoride at low temperature ($-105 \sim -80°$) while C-protonated phenols were found in acids of higher strength and at higher temperature.

Hydroxy- and alkoxy-substituted benzenium ions have been studied by a number of investigators.[2] The site of protonation seemed to depend on the acid–solvent system and temperature. However, no systematic study of protonation of hydroxy(alkoxy)benzenes in different acid systems was so far attempted. Furthermore, the sites of protonation are not yet well understood. The effect of substitutents on benzenium ions were also not yet extensively studied. Isomeric ions derived from the same precursor are known (*e.g.*, C- and O-protonated anisole),[2b] but the factors (electronic and steric, as well as those of media) that control the relative amounts of isomeric ions formed were not known.

We now report a systematic study of these questions by pmr spectroscopy of ions obtained from mono- and dihydroxybenzenes and their methyl ethers. Four superacid systems were used: I, HF–SbF_5 (1:1 M:M)–SO_2ClF; II, HSO_3F–SbF_5 (1:1 M:M)–SO_2ClF, III, HSO_3F–SbF_5(4:1 M:M)–SO_2ClF; and IV, HSO_3F–SO_2ClF. In addition, protonation of phenol was carried out in weaker acids, like HF containing traces of SbF_5, in order to study both substituent and solvent effects. The nature of the extensive charge delocalization in the p-hydroxy- and methoxybenzenium ions was also studied by carbon-13 nmr spectroscopy.

Results and Discussion

The hydroxybenzene derivatives were protonated in the four different superacid systems (I–IV). Ions

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[1] Part CXXXIII: G. A. Olah, G. Liang, J. R. Wiseman, and J. A. Chong, *J. Amer. Chem. Soc.*, **94**, 4729 (1972).

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