Appendix. Relationship between Rate Equations and Mechanism

A steady-state solution of the chemical equations of Scheme I yields, after deletion of minor terms, rate eq 1 and 2, where[44]

$$k_a^* = k_2k_5/(k_{-2} + k_5) \qquad k_b^*K_{app} = \frac{K_1k_1k_5}{k_{-1}K_a}$$

$$k_c^* = k_3k_6/(k_{-3} + k_6) \qquad K_{app} = \frac{K_1(k_{-2} + k_5)}{k_{-1}}$$

$$k_d = k_1/K_a$$

$$k_e = k_{-2}k_2/(k_{-2} + k_5) \qquad k_f = k_3k_{-3}/(k_{-3} + k_6)$$

Now either the epimerization data taken separately (k_a and k_b) or the exchange data taken separately (k_e and k_d) may be used to calculate the rate ratio of the water-catalyzed hydration step (k_2) to the acid-catalyzed hydration step (k_1)

$$k_a/k_bK_a = k_2/k_1 \approx 10^{-6} \qquad (\text{assuming } K_a \approx 10^3\ M)$$

and

$$k_e/k_dK_a = k_2/k_1 \approx 10^{-6}$$

$$(\text{assuming } k_e \approx k_2;\ \text{see } k_e/k_a \text{ ratio})$$

Either *independent* calculation shows that acid-catalyzed hydration is 10^6 times faster than the water rate. This is encouraging evidence that exchange and epimerization follow a common mechanism, hopefully that of Scheme I. Similarly, $k_e/k_a = k_{-2}/k_5 \approx 5.5$, $k_1 \approx 7 \times 10^{-1}$ sec^{-1}, and $k_2 = 1.1 \times 10^{-6}$ sec^{-1}, and since $k_f/k_c = k_{-3}/k_6 \approx 140$, $k_3 \approx k_f = 7.7 \times 10^{-4}$ sec^{-1} M^{-1}, $k_2/k_3 \approx 10^{-3}$ M. These results indicate that hydration is partially rate limiting for epimerization in neutral solution; on the other hand, pseudorotation is entirely rate limiting for epimerization in strong base and acid. This is reasonable since the water-catalyzed hydration step is so inefficient compared to the acid- or base-catalyzed[45] hydration step.

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[44] In order to allow a direct comparison of the above rate terms, the observed epimerization rate constants (designated by an asterisk) were corrected for reaction of the trans isomer only

$$k_{obsd} = k_{cis} + k_{trans}$$

$$K_{eq} = (\text{trans})/\text{cis} = k_{cis}/k_{trans} \simeq 4$$

[45] Unfortunately, we find it difficult to say anything more about the base-catalyzed reaction.

Vinyl Ether Hydrolysis. IV. Catalysis in Dilute Hydrofluoric Acid Solutions[1]

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Abstract: The hydrolysis of four vinyl ethers (ethyl vinyl, phenyl isopropenyl, and methyl and ethyl cyclohexenyl) was found to be catalyzed strongly by molecular hydrofluoric acid (HF), but not at all by the hydrogen bifluoride ion (HF_2^-) present in dilute aqueous hydrofluoric acid buffers. This result agrees with the outcome of a previous investigation of the catalytic activity of aqueous hydrofluoric acid solutions, provided that an error in the earlier work is corrected, and is consistent also with the molecular structures of HF and HF_2^-. The catalytic strength of HF is in all cases nearly an order of magnitude greater than expected on the basis of Brønsted relations using carboxylic acid data; these deviations can be understood on electrostatic grounds.

In dilute aqueous solution, hydrogen fluoride ionizes as an acid (eq 1) and also associates with fluoride ion

$$HF \rightleftharpoons H^+ + F^- \qquad (1)$$

(eq 2); these solutions therefore contain three acidic

$$HF + F^- \rightleftharpoons HF_2^- \qquad (2)$$

species, HF, H^+, and HF_2^-. This complexity, however, might still leave the catalytic activity of these solutions fairly simple if HF_2^- were to be as poor a proton donor as expected on the basis of its molecular structure: it is a linear, negatively charged species with hydrogen at the center,[2] from which it should be fairly difficult to remove a proton, much harder than from HF. Nevertheless, in an earlier investigation of this matter,[3] the conclusion was reached that HF and HF_2^- have comparable acid catalytic strengths.

In a preliminary account of the present work,[4] we pointed out that this previous conclusion was based upon a faulty kinetic analysis; we also reported that HF catalyzes the hydrolysis of ethyl vinyl ether but HF_2^- does not. That work is described here in detail, and additional data for the hydrolysis of several other vinyl ethers by HF are presented. The latter are of special interest in view of the fact that HF gives up a proton without undergoing structural reorganization, which might make it a better catalyst than other acids of similar pK_a whose ionization is accompanied by extensive changes.[5]

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[1] (a) This research was supported by grants (GP 6580 and GP 9253) from the National Science Foundation; (b) part III: A. J. Kresge, H. L. Chen, Y. Chiang, E. Murrill, M. A. Payne, and D. S. Sagatys, *J. Amer. Chem. Soc.*, **93**, 413 (1971).

[2] K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," 2nd ed, Wiley, New York, N. Y., 1970, pp 82–84; W. C. Hamilton and J. A. Ibers, "Hydrogen Bonding in Solids," W. A. Benjamin, New York, N. Y., 1968, pp 108–113.

[3] R. P. Bell and J. C. McCoubrey, *Proc. Roy. Soc., Ser. A*, **234**, 192 (1956).

[4] A. J. Kresge and Y. Chiang, *J. Amer. Chem. Soc.*, **90**, 5309 (1968).

Table I. Rates of Hydrolysis of Ethyl Vinyl Ether in Aqueous Hydrofluoric Acid at 24.9° [a]

$10^2[HF]_s$ [b]	$10^2[HF]$ [c]	$10^2[H^+]$ [d]	$10^2[HF_2^-]$ [c]	10^2k_{obsd}, sec^{-1}	10^2k_{HF},[e] M^{-1} sec^{-1}
7.38	6.4	0.805 (0.81)	0.175	1.84, 1.85, 1.85	6.80, 6.85, 6.85
8.60	7.5	0.885 (0.89)	0.215	2.05, 2.06, 2.08	6.67, 6.80, 7.00
17.0	15.1	1.43 (1.45)	0.525	3.51, 3.51	6.78, 6.78
25.4	22.6	1.94 (2.03)	0.920	4.84, 4.87	6.52, 6.65
29.5	26.2	2.19 (2.29)	1.11	5.50, 5.52, 5.60	6.38, 6.45, 6.75
					Av 6.71 ± 0.05[f]

[a] Ionic strength variable (fixed by extent of dissociation of HF). [b] Stoichiometric concentrations. [c] Actual (calculated) concentrations. [d] Actual concentrations; values in parentheses were determined experimentally using 2,4-dichloroaniline as an acid–base indicator and the others were calculated as described in text. [e] Calculated according to $k_{HF} = (k_{obsd} - k_{H^+}[H^+])/[HF]$ using 1.75 M^{-1} sec^{-1} as k_{H^+}. [f] Standard deviation of the mean.

Table II. Rates of Hydrolysis of Ethyl Vinyl Ether in Aqueous Hydrofluoric Acid–Sodium Fluoride Buffer Solutions at 24.9° [a]

				10^3k, sec^{-1}	
$10^2[HF]_s$ [b]	$10^2[HF]$ [c]	$10^2[H^+]$ [c]	$10^2[HF_2^-]$ [c]	k_{obsd}	$k_{obsd} - (k_{H^+}[H^+] + k_{HF}[HF])$ [d]
			$[HF]_s/[NaF]_s$ [b] $= 0.200$		
1.00	0.88	0.0214	0.105	0.975, 0.975	0.011, 0.011
2.01	1.46	0.0173	0.535	1.31, 1.33	0.03, 0.05
3.02	1.95	0.0150	1.05	1.62, 1.63	0.05, 0.06
4.02	2.35	0.0135	1.66	1.81, 1.81, 1.82	0.00, 0.00, 0.01
			$[HF]_s/[NaF]_s$ [b] $= 0.635$		
3.17	2.62	0.0711	0.478	3.04, 3.06, 3.07	0.04, 0.06, 0.07
6.35	4.73	0.0691	1.55	4.38, 4.38	0.00, 0.00
9.52	6.45	0.0666	3.00	5.42, 5.43	−0.07, −0.06
12.7	7.93	0.0642	4.71	6.45, 6.47	0.00, 0.02

[a] Ionic strength maintained at 0.20 M with NaCl. [b] Stoichiometric concentrations. [c] Actual (calculated) concentrations. [d] Calculated using $k_{H^+} = 1.75$ M^{-1} sec^{-1} and $k_{HF} = 6.71 \times 10^{-2}$ M^{-1} sec^{-1}.

Experimental Section

Materials. Ethyl vinyl ether was obtained commercially (Aldrich Chemical Co.) and other kinetic substrates were prepared as described previously.[1b] Hydrofluoric acid solutions were made by diluting the 48% acid (Fisher Chemical Co., Reagent Grade) and then determining exact concentrations by acidimetric titration. Sodium fluoride–hydrogen fluoride buffers were prepared by combining hydrofluoric acid and sodium fluoride (Fisher, Certified) solutions and also by partially neutralizing hydrofluoric acid solutions with sodium hydroxide; the two methods gave identical results.

All solutions containing hydrogen fluoride were prepared and stored in, and transferred directly from, polyethylene dropping bottles.

Kinetics. Rates of hydrolysis were measured spectroscopically by following the decrease in absorbance of vinyl ether at 220 nm.[1b,6] An optical cell with Kel-F body and sapphire windows[7] was constructed for this purpose. Rate constants were evaluated graphically using infinity points measured after 8–10 half-lives.

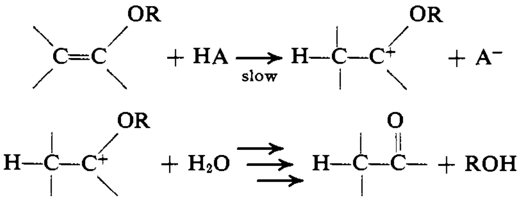
Results and Discussion

Lack of Catalysis by HF_2^-. All of the available evidence[1b,6,8] indicates that the hydrolysis of simple vinyl ethers proceeds through rate-determining proton transfer from a catalyzing acid to the substrate, and that this is then followed by rapid steps which give a carbonyl compound and an alcohol as ultimate products (eq 3). The reaction is subject to general acid catalysis and obeys the rate law given as eq 4; for hydrofluoric acid solutions, this reduces to the particular form shown as eq 5. It follows from the mechanism of eq 3 that the various catalytic coefficients in this rate

$$\frac{d[\text{vinyl ether}]}{[\text{vinyl ether}]dt} = k_{obsd} = \sum_i k_{HA_i}[HA_i] \qquad (4)$$

$$k_{obsd} = k_{H^+}[H^+] + k_{HF}[HF] + k_{HF_2^-}[HF_2^-] \qquad (5)$$

law measure rates of proton transfer from the catalyst acids directly.



(3)

The catalytic coefficient k_{H^+} may be determined in experiments using completely dissociated acids, and it is in fact available from our previous work[1b] on the substrates investigated here. The other two terms of eq 5 can be evaluated by first making measurements in solutions prepared from hydrofluoric acid alone, in which the concentration of HF_2^- is low, and then in solutions containing added fluoride ion, in which the concentrations of HF and HF_2^- can be made to be comparable.

The results of measurements made on ethyl vinyl ether in solutions prepared from hydrofluoric acid alone are presented in Table I and in those prepared from hydrofluoric acid plus sodium fluoride, in Table II. The actual concentrations of solution species in these reaction mixtures were calculated using published values[9] of the equilibrium constants for dissociation (eq 1) and

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(5) R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959, pp 171-175.

(6) A. J. Kresge and Y. Chiang, *J. Chem. Soc. B*, 53, 58 (1967).

(7) M. Kilpatrick and J. G. Jones in "The Chemistry of Non-Aqueous Solvents," Vol. II, J. J. Lagowski, Ed., Academic Press, New York, N. Y., 1967, Chapter 2.

(8) D. M. Jones and N. F. Wood, *J. Chem. Soc.*, 5400 (1964); P. Salomaa, A. Kankaanpera, and M. Lajunen, *Acta Chem. Scand.*, **20**, 1790 (1966); P. Salomaa and A. Kankaanpera, *ibid.*, **20**, 1802 (1966); T. Fueno, I. Matsumura, T. Okuyama, and J. Furukawa, *Bull. Chem. Soc. Jap.*, **41**, 818 (1968); G. Lienhard and T. C. Wang, *J. Amer. Chem. Soc.*, **91**, 1146 (1969); A. J. Kresge and H. J. Chen, *ibid.*, **94**, 2818 (1972).

(9) H. H. Broene and T. De Vries, *ibid.*, **69**, 1644 (1947).

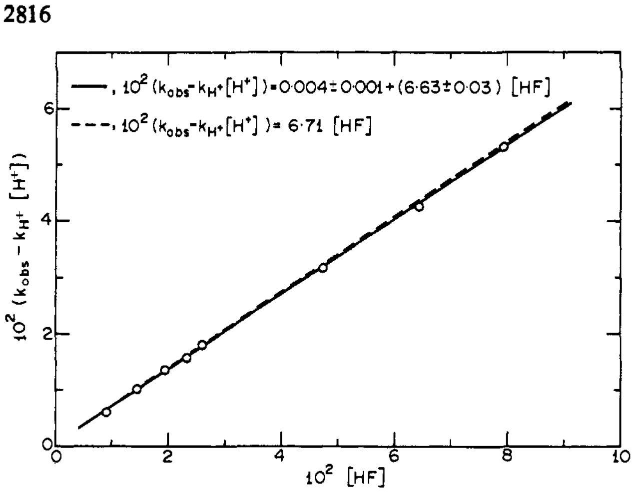

Figure 1. The hydrolysis of ethyl vinyl ether in aqueous HF–NaF buffers: comparison of experimentally determined specific rates of reaction (solid line) with rates calculated on the basis of no catalysis by HF_2^- (broken line).

association (eq 2) of HF (eq 6 and 7). These equations

$$K_1 = [H^+][F^-]/[HF] = 6.71 \times 10^{-4} \quad (6)$$

$$K_2 = [HF_2^-]/[HF][F^-] = 3.96 \quad (7)$$

are each quadratic in the quantities of interest, and combination of the two, which is necessary for solution, gives a cubic expression; this was solved directly with the aid of a programmable electronic desk calculator (Wang Model 362). The position of the association equilibrium (eq 2) was taken to be independent of ionic strength, but salt effects on the acid dissociation of HF (eq 1) were accounted for by estimating ionic activity coefficients according to eq 8.[3,10] In the experiments using solutions with added fluoride ion,

$$\log f_{\pm} = \frac{-0.50\mu^{1/2}}{1 + \mu^{1/2}} + 0.1\mu \quad (8)$$

ionic strength (μ) was held constant through the addition of sodium chloride, but no inert electrolyte was added to the solutions prepared from hydrofluoric acid alone (Table I). The ionic strength of these solutions was therefore fixed by the extent of ionization of HF, and was consequently variable; in these cases, the calculations were done in an iterative fashion until self-consistent sets of ion concentrations and ionic strengths were obtained.

This method of determining solution composition was checked in a few cases by using 2,4-dichloroaniline as an acid–base indicator to measure hydrogen ion concentrations. The agreement between the results of these experiments and the calculated values was on the whole very good (Table I, column 4).

Inspection of Table I shows that the concentration of HF_2^- in the solutions which were prepared from hydrofluoric acid alone is only a few per cent of the concentration of HF; in these solutions, therefore, hydrolysis through catalysis by HF_2^- might make a negligible contribution to k_{obsd}, and might be neglected, even if HF_2^- were an effective proton donor. That this is indeed the case is indicated by the fact that values of k_{HF} calculated on this basis, *i.e.*, as ($k_{obsd} - k_{H^+}[H^+]$)/[HF], are constant (Table I, column 6); what little variation there is is random and cannot be correlated with the regular change in the ratio $[HF_2^-]/[HF]$ (= 0.027 to 0.042) which occurs from the top to the bottom of Table I.

It may be seen in Table II, on the other hand, that the solutions prepared from hydrofluoric acid plus sodium fluoride do contain appreciable amounts of HF_2^-; the ratio $[HF_2^-]/[HF]$ ranges from 0.12 to 0.71 for the first series of experiments with buffer ratio = 0.2 and from 0.18 to 0.59 for the second series with buffer ratio = 0.6. In these solutions, therefore, catalysis by HF_2^- would make a significant contribution to k_{obsd} if $k_{HF_2^-}$ and k_{HF} were comparable in magnitude, as claimed.[3] But even here, rates of hydrolysis can be accounted for precisely by reaction through H^+ and HF alone. This is evident from Figure 1 where $k_{obsd} - k_{H^+}[H^+]$ is plotted against [HF]; the full line of slope $(6.63 \pm 0.03) \times 10^{-2}\ M^{-1}\ sec^{-1}$ results from least-squares analysis of the data, whereas the broken line was drawn with slope equal to 6.71×10^{-2}, the value of k_{HF} obtained in the previous set of experiments (Table I). The lack of catalysis by HF_2^- is also apparent from the remainders obtained when rates of reaction through H^+ and HF are subtracted from k_{obsd} (Table II, column 6); these fluctuate within a per cent or two of zero and bear no sensible relationship to the concentration of HF_2^-. In fact, least-squares analysis of the relationship between these remainders and HF_2^- concentrations gives a negative value to $k_{HF_2^-}$ with an uncertainty twice its absolute magnitude: $(-1.4 \pm 2.3) \times 10^{-3}\ M^{-1}\ sec^{-1}$. Thus, if catalysis by HF_2^- is present at all in the hydrolysis of ethyl vinyl ether, the catalytic strength of HF_2^- cannot be more than *ca.* 3% that of HF.

This situation contrasts sharply with the conclusion reached in the only other reported study of acid catalysis in dilute hydrofluoric acid solutions.[3] In that work, two general acid catalyzed reactions, the iodination of acetone and the iodination of acetonylacetone, were examined, and in each case comparable catalytic strengths for HF and HF_2^- were found: $k_{HF} = 6.8 \times 10^{-7}$ and $k_{HF_2^-} = 6.4 \times 10^{-7}\ M^{-1}\ sec^{-1}$ for acetone and $k_{HF} = 7.4 \times 10^{-7}$ and $k_{HF_2^-} = 1.0 \times 10^{-6}\ M^{-1}\ sec^{-1}$ for acetonylacetone. Close scrutiny, however, shows that one of the expressions used to calculate solution compositions in this work was in error (the second term on the right-hand side of eq 5 in ref 3 should have had the coefficient $^1/_2$ rather than $^1/_4$). This had the effect of overestimating H^+ concentrations in the more acidic solutions. When this mistake is corrected, k_{HF} for both reactions is increased significantly (to $8.0 \times 10^{-7}\ M^{-1}\ sec^{-1}$ for acetone and $10.5 \times 10^{-7}\ M^{-1}\ sec^{-1}$ for acetonylacetone), and this in turn reduces the amount of reaction which can be attributed to HF_2^-. The result is that catalysis by HF_2^- vanishes completely in the acetonylacetone reaction and drops to a level which is probably not experimentally significant in the case of acetone. Thus, the results of this earlier study are, in fact, consistent with those of the present investigation in showing HF_2^- to be a poorer proton donor than HF.

Catalytic Strength of HF. Once catalysis by HF_2^- is known to be negligible in relation to that by HF, solutions prepared from hydrofluoric acid plus sodium fluoride, *i.e.*, hydrofluoric acid buffers, become the

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(10) C. W. Davies, *J. Chem. Soc.*, 2093 (1938).

Table III. Rates of Hydrolysis of Other Vinyl Ethers in Hydrofluoric Acid Buffers at 25.0°

$10^2[HF]_s$[a]	$10^2[HF]$[b]	$10^4[H^+]$[b]	10^3k_{obsd}, sec^{-1}	$10k_{HF}$, M^{-1} sec^{-1}
		Phenyl Isopropenyl Ether, $[HF]_s/[Na]_s$[a] = 0.40[c]		
4.27	3.14	4.36	9.95, 9.60, 10.0	2.34, 2.23, 2.35
5.97	4.04	4.14	11.8, 11.6	2.30, 2.25
8.53	5.25	3.89	14.2, 14.0, 13.7	2.25, 2.22, 2.16
			Av	2.26 ± 0.02[e]
		Phenyl Isopropenyl Ether, $[HF]_s/[Na]_s$[a] = 0.20[d]		
2.00	1.45	2.07	4.90, 4.97, 4.95, 4.83, 4.80	2.52, 2.57, 2.56, 2.48, 2.46
4.00	2.33	1.72	7.04, 7.02, 6.76	2.58, 2.57, 2.46
6.00	2.95	1.48	7.52, 7.54, 7.52, 7.50, 7.80	2.25, 2.25, 2.25, 2.24, 2.34
8.00	3.40	1.30	8.45, 8.48, 8.65, 9.00, 9.00	2.26, 2.27, 2.32, 2.42, 2.42
			Av	2.40 ± 0.03[e]
		Phenyl Isopropenyl Ether, $[HF]_s/[NaF]_s$[a] = 0.10[d]		
1.00	0.72	1.00	2.22, 2.21, 2.46, 2.38	2.25, 2.24, 2.58, 2.47
2.00	1.14	0.80	3.20, 3.27	2.38, 2.44
3.00	1.43	0.68	3.86, 3.83	2.41, 2.39
4.00	1.65	0.60	4.31, 4.32, 4.16	2.39, 2.40, 2.30
			Av	2.39 ± 0.03[e]
			Grand mean	2.33 ± 0.02[e]
		Methyl Cyclohexenyl Ether, $[HF]_s/[NaF]_s$[a] = 0.107[d]		
1.28	0.88	1.03	19.1, 18.9, 19.1	16.9, 16.6, 16.9
2.14	1.23	0.87	24.4, 24.3	16.8, 16.8
2.99	1.47	0.76	26.8, 26.7, 26.8	16.1, 16.0, 16.1
4.27	1.74	0.63	30.1, 30.0, 30.3	15.8, 15.6, 15.9
			Av	16.3 ± 0.2[e]
		Ethyl Cyclohexenyl Ether, $[HF]_s/[NaF]_s$[a] = 0.075[d]		
0.70	0.51	0.77	24.6, 24.4, 24.2, 24.4	47.0, 46.6, 46.2, 46.6
1.01	0.67	0.70	30.6, 29.6, 30.6, 29.6	45.0, 43.5, 45.0, 43.5
			Av	45.4 ± 0.5[e]

[a] Stoichiometric concentrations. [b] Actual (calculated) concentrations. [c] Ionic strength maintained at 0.20 M with NaCl. [d] Ionic strength maintained at 0.40 M with NaCl. [e] Standard deviation of the mean.

media of choice for determining HF catalytic coefficients. Table III presents the results of experiments done in such solutions using three additional vinyl ethers. The data cover a wide range of solution composition, and the fact that kinetic analysis on the basis of reaction through HF and H^+ alone gives nicely constant values of k_{HF} affords additional evidence for the absence of significant catalysis by HF_2^-.

The HF catalytic coefficients obtained here for these four vinyl ether hydrolyses are of further interest in that they can be compared with rate constants for catalysis by acids of a different kind. Brønsted relations based on carboxylic acid data have been constructed[1b] for each of these vinyl ether hydrolysis reactions, and these correlations may be used to interpolate specific rates for a hypothetical carboxylic acid of the same pK_a as HF. The results (Table IV) show that when effects of acid strength are removed in this way, HF is a substantially better catalyst than RCO_2H.

It has been suggested[5] that this difference is the result of the fact that all of the negative charge generated in the catalyst during proton separation from HF remains localized on the fluorine atom, whereas a part of the charge formed in proton removal from RCO_2H is dispersed onto the more distant oxygen. It can be shown that the former situation leads to a steeper initial rise in energy with increasing distance of separation than does the latter; thus, more energy is required to move a proton a short distance from RCO_2H than from HF. This difference may be understood in terms of the electrostatic stabilization of the two opposite charges in the separated state; this stabilization will be greater in the case of HF because the charges are closer together.

Table IV. Comparison of Catalytic Strengths of HF and RCO_2H

Reaction	Log k_{HF}	Log k_{RCO_2H}[a]	Dif
Hydrolysis of ethyl vinyl ether	−1.17	−1.76	0.80
Hydrolysis of phenyl isopropenyl ether	−0.63	−1.22	0.78
Hydrolysis of methyl cyclohexenyl ether	0.21	−0.34	0.75
Hydrolysis of ethyl cyclohexenyl ether	0.66	−0.10	0.93
Iodination of acetone	−6.10[b]	−6.64	0.54
Iodination of acetonylacetone	−5.98[b]	−6.64	0.66

[a] Catalytic coefficients for carboxylic acid with pK_a = 3.17 = pK_a(HF) calculated using appropriate Brønsted relations (ref 1b and 3). [b] Recalculated values.