Phenyliminodiethanol Dibenzoate (XXIV).—A mixture of 9.1 g (5 × 10^{-2} mol) of phenyliminodiethanol (Matheson Coleman and Bell), 15.5 g (0.12 mol) of benzoyl chloride and 50 ml of pyridine was heated to 50° for 3 hr. The reaction mixture was poured onto ice water; the solid was collected and recrystallized from 400 ml of methanol to give 17.2 g (88%) of phenyliminodiethanol dibenzoate, mp 71.5° (lit.[13] 77°).

Anal. Calcd for $C_{24}H_{23}NO_4$: C, 74.02; H, 5.95; N, 3.59; O, 16.43. Found: C, 74.06; H, 6.09; N, 3.62; O, 16.18.

p-Anisyliminodiethanol Dibenzoate (XXV).—A mixture of *p*-anisyliminodiethanol (10.6 g, 5 × 10^{-2} mol), benzoyl chloride (15.5 g; 0.12 mol) and 50 ml of pyridine gave *p*-anisyliminodiethanol dibenzoate by the same procedure used for XVII. One crystallization gave 10.6 g (50%) of XVIII, mp 62.4°.

Anal. Calcd for $C_{25}H_{25}NO_5$: C, 71.58; H, 6.01; N, 3.34; O, 19.07. Found: C, 70.87; H, 6.04; N, 3.38; O, 19.65.

Charge-Transfer Complexes. Materials.—The aromatic hydrocarbons (Table II) were used as received from the Aldrich Chemical Company. The syntheses of the aromatic monoamines are described above while the preparation of the phenyliminodiethanol polymers was previously described.[3b] TMPD was obtained from Matheson Coleman and Bell (MCB), converted to the dihydrochloride, recrystallized from 2-propanol,

(13) B. C. Mc Kusick, R. E. Heckert, T. L. Cairns, D. D. Coffman, and H. F. Mower, *J. Amer. Chem. Soc.* **80**, 2806 (1958).

neutralized with sodium hydroxide and finally sublimed. It melted at 50°.[12]

The synthesis of the fluorene acceptors (Vc–IXc) are described above. Chloranil was obtained from MCB and recrystallized from benzene, mp 287°. DDQ was obtained from Aldrich Chemical Company and recrystallized from chloroform, mp 201°.

Spectra.—All measurements were made with a Cary 14 spectrophotometer using 1,1,2,2-tetrachloroethane of Spectrograde quality as solvent.

Equilibrium in the Addition of Hydrogen Peroxide, Water, and Methanol to Acetone[1a]

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Equilibrium constants of 5.3 × 10^{-2}, 2.5 × 10^{-5}, and 1.9 × 10^{-4} M^{-1} have been determined for the addition of hydrogen peroxide, water, and methanol to acetone. These equilibrium constants and values from the literature for hydroxylamine, hydrogen cyanide, and bisulfite ions give a satisfactory linear logarithmic plot against the γ of Sander and Jencks.

In connection with a study of the basicity of various nucleophilic reagents toward carbon,[2] equilibrium constants for the addition of hydrogen peroxide, water, and methanol to acetone were needed. These constants were determined by proton magnetic resonance (pmr) measurements.

Results

The addition of hydrogen peroxide to aqueous solutions of acetone gave rise to a new pmr peak at about τ 8.64 in addition to the acetone peak at about 7.84 ppm. The area of this new peak relative to that of the acetone peak grew over a period of hours, especially at high concentrations of hydrogen peroxide and acetone. This growth was more rapid when the solutions were made 0.001 M in perchloric acid but became unobservable in the presence of 0.1 M sodium acetate. By analogy to the fact that hemiacetal formation is both acid and base catalyzed and is fairly rapid in neutral solutions, whereas acetal formation is only acid catalyzed, we assumed that equilibrium in the addition of hydrogen peroxide to acetone had already been established by the

$$Me_2CO + H_2O_2 \rightleftharpoons Me_2COOH \quad (1)$$
$$\underset{OH}{}$$
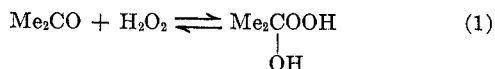
time (about 1 hr) the first pmr measurements were made. The subsequent, slower, acid-catalyzed reaction is thought to consist of the formation of 2,2-bis(hydroperoxy)propane, as shown in eq 2. In addition,

$$Me_2CO + 2H_2O_2 \rightleftharpoons Me_2C(OOH)_2 \quad (2)$$

various other peroxide derivatives of acetone[3] were probably being formed to at least some extent. This interpretation of our results is consistent with the chemical shifts to be expected for the monohydroperoxy and bishydroperoxy products shown in eq 1 and 2. The new peak absorbs 0.80 ppm upfield from acetone. The methyl peaks for paraldehyde and acetaldehyde diethyl acetal appear 0.80 and 0.88 ppm, respectively, upfield from the methyl peak of acetaldehyde.[4] Since a hydroperoxy group has essentially the same effect as a hydroxy group on the chemical shift of a β proton,[5] the mono- and bishydroperoxy compounds would be expected to have about the same chemical shift. That this is the case is further supported by the observation to be described later in this paper that the pmr peaks

(1) (a) This investigation was supported in part by Grant GP-7629 from the National Science Foundation. (b) The Ohio State University. (c) NSF Undergraduate Research Participant, summer, 1964.

(2) J. Hine and R. D. Weimar, Jr. *J. Amer. Chem. Soc.*, **87**, 3387 (1965).

(3) *Cf.* N. A. Milas and A. Golubović, *ibid.*, **81**, 6461 (1959), and references listed therein.

(4) N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, "High Resolution NMR Spectra Catalog," Vol. 1, Varian Associates, Palo Alto, Calif., 1962, No. 6, 143; N. S. Bhacca, D. P. Hollis, L. F. Johnson, and E. A. Pier, "High Resolution NMR Spectra Catalog," Vol. 2, Varian Associates, Palo Alto, Calif., 1963, no. 474.

(5) W. D. Wilk, A. L. Allred, B. A. Koven, and J. A. Marshall, *J. Chem. Soc. B*, 565 (1969).

for the hydrate and the methyl hemiacetal of acetone are 0.78 ppm upfield from that for acetone. It is therefore not surprising that the formation of the bishydroperoxide is not accompanied by the formation of a new pmr peak but merely by the growth (with some broadening, however) of the peak attributed to the monohydroperoxide. If reaction 1 is the only process that is occurring to a significant extent, its equilibrium constant (K) may be calculated from eq 3, where $[H_2O_2]_0$

$$K = \frac{1 - f}{f([H_2O_2]_0 - f[Me_2CO]_0)} \quad (3)$$

and $[Me_2CO]_0$ are the concentrations of hydrogen peroxide and acetone originally added, and f is equal to the area of the peak at about τ 8.65 divided by the sum of the areas of the peaks at 8.65 and 7.85 ppm. Values of K calculated from measurements on solutions 0.1 M in sodium acetate are listed in Table I. No clear trends

TABLE I

EQUILIBRIUM IN THE ADDITION OF HYDROGEN PEROXIDE
TO ACETONE IN AQUEOUS SOLUTION AT 35°[a]

$[Me_2CO]_0$, M	$[H_2O_2]_0$, M	K, M^-	K', N^{-1}
2.74	1.89	0.061	0.028
5.48	1.89	0.044	0.020
4.11	2.52	0.069	0.030
5.48	2.52	0.070	0.030
2.74	3.15	0.047	0.022
5.48	3.15	0.042	0.020
	Av	0.056 ± 0.011	0.025 ± 0.004

[a] Solutions contained 0.1 M sodium acetate to prevent reaction 2. Each equilibrium constant is the average of two to four measurements.

accompany changes in concentrations of acetone and hydrogen peroxide, perhaps because of the fairly large experimental uncertainty in the values of K.

The conditions that sufficed to establish equilibrium in reaction 1 might also bring about equilibrium in the addition of the hydroperoxy group of the product of reaction 1 to another molecule of acetone as shown in eq 4. We have no convincing evidence as to whether

$$Me_2COOH + Me_2CO \rightleftharpoons Me_2COOCMe_2 \quad (4)$$
$$\ \ || |$$
$$OH OH\ \ OH$$
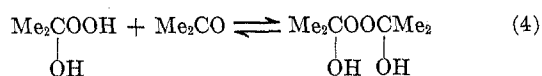
reaction 4 is taking place or not, but its probable effect on our determination of K may be estimated as follows. Let us assume that the oxygen-bound hydroxy group in $Me_2C(OH)OOH$ has the same tendency to add to acetone that such a group in hydrogen peroxide does, neglecting statistical effects.[6] Then we may define an equilibrium constant for the addition of oxygen-bound hydroxy groups to acetone as shown in eq 5. In eq 5,

$$K' = \frac{[Me_2C(OH)OO-]}{[Me_2CO][-OOH]} \quad (5)$$

[-OOH] is the concentration, in equivalents per liter, of oxygen-bound hydroxy groups, and $[Me_2C(OH)OO-]$ is that of peroxy-complexed acetone. In terms of the symbols used in eq 3, K' may be calculated as shown in eq 6. Values of K' are also given in Table I. If the

$$K' = \frac{1 - f}{f(2[H_2O_2]_0 - f[Me_2CO]_0)} \quad (6)$$

assumptions on which the calculation of K' was based are correct, then K must equal $2K'$ since K refers to hydrogen peroxide, which has two peroxy OH groups that can add. Thus the assumption that K' is a constant leads to the value 0.050 M^{-1} for K, a value only 10% smaller than the one calculated with the complete neglect of reaction 4.

The values of K calculated from data on solutions containing no sodium acetate usually increased with time, and after 24 hr, values as large as 0.5 M^{-1} were obtained.

When the pmr spectra of aqueous solutions containing about 20% acetone by volume were run at high amplitude on a 60-MHz instrument, a peak was noted about 47 Hz (0.78 ppm) upfield from the principal acetone peak. This peak was considerably smaller than the ^{13}C satellite peaks, 65 Hz on either side of the acetone peak. There was no matching peak 0.78 ppm downfield from acetone, and the peak was also observed in the pmr spectrum of 20% solutions of acetone in deuterium oxide. For the reasons described in discussing the hydrogen peroxide adducts of acetone, this chemical shift is plausible for acetone hydrate (2,2-propanediol). We therefore utilized the fact that the spectrum of an aldehyde hydrate may be fused with that of the corresponding aldehyde in aqueous solution by the addition of acid to speed the hydration–dehydration reactions.[7] In the presence of 0.0001 M perchloric acid the acetone hydrate peak could no longer be detected.

To be sure that the difference between the acetone peak and the peak we were attributing to the hydrate was a chemical shift rather than some sort of coupling, the pmr spectra of 20% solutions of acetone in protium oxide and deuterium oxide were run on a 100-MHz spectrometer. The new peak was now found on the other side of the upfield ^{13}C satellite of acetone, 78 Hz (0.78 ppm) upfield from acetone.

In order to determine the equilibrium constant for hydration, the area of the peak due to acetone hydrate was compared with that of the nearby ^{13}C satellite, whose area was assumed to be 0.55% that of the acetone peak. (The natural abundance of ^{13}C is 1.1%.) Measurements on the 60-MHz spectra of 20% solutions gave 0.15 ± 0.07% as the extent of hydration of the acetone, but measurements at 100 MHz gave 0.11 ± 0.03% in protium oxide and 0.09 in one set of measurements in deuterium oxide solution. The values at 100 MHz are based on larger and more reproducible peaks and are therefore believed to be more reliable. The equilibrium constant for hydration in 80% protium oxide corresponds to 0.14 ± 0.04% hydration in 100% protium oxide.

The pmr spectrum of a 28 vol % solution of acetone in methanol was found to contain a peak 0.78 ppm upfield from acetone. For reasons of the type described in consideration of addition of water and hydrogen peroxide to acetone, this peak was attributed to the hemiacetal. Its area was 0.59 ± 0.07 that of the nearby ^{13}C satellite of acetone, and therefore the equilibrium constant for the addition of methanol to acetone is (19 ± 2) $\times$ 10^{-5} M^{-1}. When about 1.2 vol % of acetone was dissolved in methanol and ultraviolet measurements were made quickly at 25°, the absorbance at 2700 Å was found to decrease rapidly (half-life about 15 sec).

(6) In view of the possibility of steric effects, this assumption seems to give a reasonable maximum for the probable importance of reaction 4.

(7) *Cf.* J. Hine and J. G. Houston, *J. Org. Chem.*, **30**, 1328 (1965).

Extrapolation of measured absorbance values to zero time gave 0.44 ± 0.10% as the extent of the decrease, corresponding to an equilibrium constant of (18 ± 4) × 10^{-5} M^{-1}.

Discussion

The equilibrium constants for addition to acetone obtained in this study are listed in Table II; also listed

TABLE II
EQUILIBRIUM CONSTANTS FOR ADDITION TO ACETONE[a]

Addend	K, M^{-1}	γ[b]
H_2O[c]	2.5×10^{-5}	-3.58
MeOH[d]	1.9×10^{-4}	-2.22
H_2O_2[e]	5.3×10^{-2}	-0.64
H_2NOH[f,g]	1.0	1.24
HCN[h]	14	2.44
HSO_3^-[i]	1.5×10^2	4.02

[a] In aqueous solution at 35° unless otherwise noted. [b] From ref 8. [c] At 33°. [d] In methanol. [e] An average of the two equally plausible values, 0.056 and 0.050 M^{-1}, is listed. [f] W. P. Jencks, *J. Amer. Chem. Soc.*, 81, 475 (1959). [g] At 25°. [h] D. P. Evans and J. R. Young, *J. Chem. Soc.*, 1310 (1954). [i] Extrapolated from data of ref 9 at 0, 20, and 30°.

are values determined by other investigators. Sander and Jencks have measured equilibrium constants for a number of additions to aldehydes and have suggested the parameter γ as a measure of the ability of a reagent to add to a carbonyl group.[8] Numerical values of γ were obtained from the defining equation

$$\gamma_{HX} = \log \frac{K_{HX}}{K_{MeNH_2}}$$

where K_{HX} and K_{MeNH_2} are equilibrium constants for the addition of the reagent in question and methylamine to pyridine-4-carboxaldehyde in water at 25°. In Figure 1 is a plot of the values of log K from Table II *vs.* γ. The K value for addition of hydrogen peroxide was divided by a statistical factor of two in accord with the practice of Sander and Jencks. The points give fairly good agreement with the least-squares line shown. The slope of this line (0.93) would be 0.96 for data at 25° if all the entropies of addition were identical. The actual deviation of the points from a straight line may be smaller than that shown. The point for bisulfite, which is low, was taken from the data of Gubareva,[9] whose equilibrium constant for benzaldehyde is stated by Sousa and Margerum[10] to be too low (by a factor of more than fivefold) because of dissociation of the adduct during titration of the bisulfite ions. Since the bisulfite addition compound of acetone dissociates about half as fast as the one derived from benzaldehyde,[11] the reported K for acetone[9] may also be too low, but probably by a smaller factor than that found for benzaldehyde.[10] The point for hydroxylamine is too high, but this is the only point not determined at 35 ± 2° and it would probably be lower at that temperature.

The equilibrium constant we have observed for the addition of methanol to acetone is smaller by a factor of about 800 than the value reported in dioxane at 26 ±
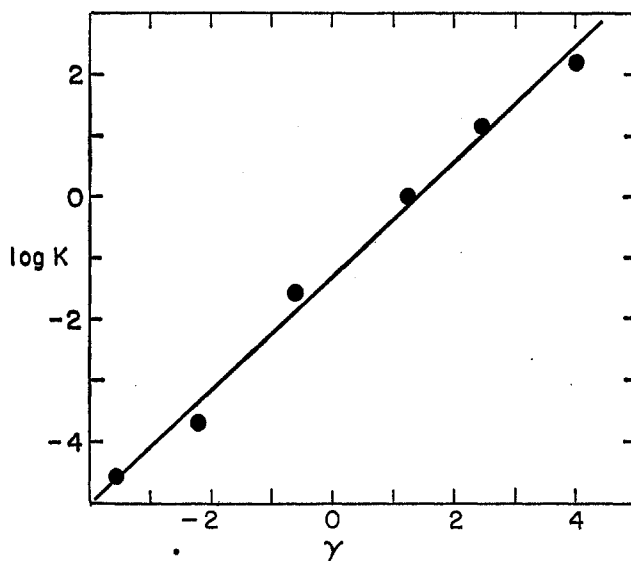
(8) E. G. Sander and W. P. Jencks, *J. Amer. Chem. Soc.*, 90, 6154 (1968).
(9) M. A. Gubareva, *Zh. Obshch. Khim.*, 17, 2259 (1947); *Chem. Abstr.*, 42, 4820a (1948).
(10) J. D. Sousa and J. D. Margerum, *J. Amer. Chem. Soc.*, 82, 3013 (1960).
(11) D. A. Blackadder and C. Hinshelwood, *J. Chem. Soc.*, 2720 (1958).

Figure 1.—Log–log plot of equilibrium constants for addition to acetone at 35° *vs.* those for addition to pyridine-4-carboxaldehyde at 25°.

1°.[12] However, the measurements in dioxane were made by the method of Wheeler,[13] in which an acid catalyst was used, and Kubler and coworkers have shown that under the conditions used, the disappearance of aldehyde or ketone is due largely to the formation of an acetal rather than a hemiacetal.[14,15] Therefore, we think that our value for methanol is more reliable. The fact that the point for methanol falls somewhat below the line in Figure 1 may be due to a solvent effect or to steric hindrance. We believe that the number of compounds studied is not enough to show whether there are certain categories of reagents that give deviations from a plot of log K *vs.* γ, as was found to be the case for formaldehyde.[8]

Experimental Section[16]

Addition of Hydrogen Peroxide.—Reagent acetone and "30%" hydrogen peroxide solutions were used, the strength of the latter being determined by refractive index measurements and by permanganate titration with satisfactory agreement. Pmr peak areas were measured by electronic integration. Each of the equilibrium constants in Table I is the result of two to four measurements made at various times between 1 and 48 hr after the solutions were mixed; no tendency of the equilibrium constant to drift was noted.

Ultraviolet measurements at about 2700 Å on about 1 M aqueous solutions of acetone and hydrogen peroxide using cells with 1-mm path lengths showed that the absorbance was smaller than that which would be expected from the amounts of acetone and hydrogen peroxide that had been added. This difference between observed and "expected" absorbance was larger in solutions 0.001 M in perchloric acid than in solutions 0.001 M in sodium bicarbonate. The fact that the absorbance of the hydrogen peroxide solutions was comparable with that of acetone solutions of about the same strength complicated the quantitative.

(12) J. M. Jones and M. L. Bender, *J. Amer. Chem. Soc.*, 82, 6322 (1960).
(13) O. H. Wheeler, *ibid.*, 79, 4191 (1957).
(14) D. G. Kubler and L. E. Sweeney, *J. Org. Chem.*, 25, 1437 (1960).
(15) J. M. Bell, D. G. Kubler, P. Sartwell, and R. G. Zepp, *ibid.*, 30, 4284 (1965).
(16) Pmr spectra were run using Varian spectrometers, a Model A-60 with a probe temperature of 35 ± 1° and a Model HA-100 with a probe temperature of about 33°. Chemical shifts are given relative to external TMS, and their absolute values are therefore not very reliable. Ultraviolet measurements were made using a Cary spectrophotometer, Model 14 at 25 ± 1°.

interpretation of the uv data, however, and this possible method for measuring the equilibrium constant was abandoned.

Hydration of Acetone.—The pmr spectra of 20 and 30 vol % solutions of acetone in water were determined at 60 MHz. At high amplitude a peak was observed 0.78 ppm upfield from acetone. This peak, whose size was not much larger than that of the background noise in the case of the noisier spectra, was shown, by changing the spin rate, not to be a spinning side-band. Its area and that of the nearby ^{13}C satellite of acetone were determined by counting squares. The spectra at 100 Hz were run 9–10 times and the results were averaged using a computer of average transients; then the whole process was repeated. Two other spectra were run using very slow sweep, very small response, and very large spectrum amplitude.

Addition of Methanol.—Pmr measurements at 60 MHz on solutions of acetone in methanol were made in a manner analogous to that used for the aqueous solutions. In a typical uv measurement, 0.035 ml of acetone was added to 3.0 ml of methanol and absorbance measurements were made as quickly as possible at 2760 Å using an equilibrated ketone solution with an absorbance of 1.467 in the reference cell. The observed absorbance decreased from 0.808 at 16 sec to an equilibrium value of 0.803. Extrapolation to zero time gave a value of 0.813. This change of 0.010 in a total absorbance of 2.280 corresponds to 0.44%. When small amounts of hydrochloric acid were added, much larger decreases in absorbance were observed.

Effects of Fluorine Substitution upon Glycidyl Ether–Dibutylamine Reaction Rates

SCOTT A. REINES, JAMES R. GRIFFITH, AND JACQUES G. O'REAR
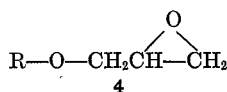
Naval Research Laboratory, Washington, D. C. 20390

Two series of fluorine-substituted glycidyl ethers have been synthesized, and their rates of reaction with dibutylamine in *t*-amyl alcohol have been measured by means of gas chromatography. The reaction was found to be second order, with dibutylamine attacking the terminal position of the epoxide ring in all cases. Fluorinated substituents generally decreased the reaction rates within each series with one outstanding exception. Rate constants and Arrhenius parameters are presented for each of the reactions studied.
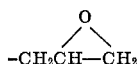
1,2-Epoxy-3-phenoxypropane (**1a**), or phenyl glycidyl ether,[1] is three to four times more reactive toward nucleophilic attack by amines in alcohol than either styrene oxide (**2**) or allylbenzene oxide (**3**).[2] It has
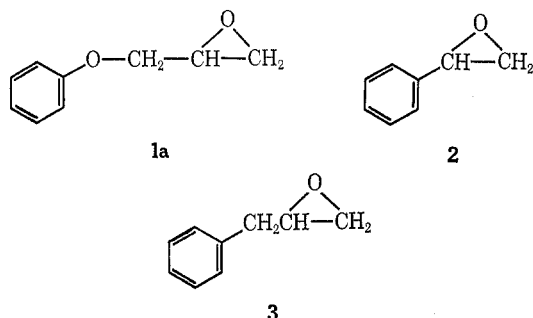
been suggested[3,4] that this increased reactivity is characteristic of all epoxides of the glycidyl ether type represented by structure **4**.

In order to determine the effects responsible for the reactivity of this type of compound, it is of interest to measure the influence of variations in the R group of **4** upon the epoxide–amine reaction rate. Although previous workers have studied the effects of solvents and the use of various nucleophiles on the rate of cleavage of the epoxide ring,[5,6] in each investigation only a single glycidyl ether was used. A comparison of the reaction rates of different glycidyl ethers under identical conditions has not to our knowledge been made.

We have prepared two series of fluorine-containing glycidyl ethers, of general structure **1** and **5**, in order to

1a, R₁ = R₂ = R₃ = R₄ = H
b, R₁ = R₃ = R₄ = H; R₂ = CF₃
c, R₁ = R₂ = R₃ = R₄ = F

5a, R₁ = R₂ = H; X = H
b, R₁ = CF₃; R₂ = H; X = H
c, R₁ = R₂ = CF₃; X = H
d, R₁ = R₂ = F; X = F

determine the effect of increasing fluorine substitution upon the rates of ring opening of these epoxides. Compounds of type **5** represent a new class of fluoro-substituted glycidyl ethers. The present paper describes the preparation of these compounds, and presents kinetic data comparing the rates of epoxide–dibutylamine reaction, in *t*-amyl alcohol, for the glycidyl ethers above.

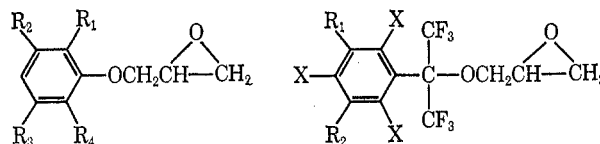(1) The term "glycidyl" is used to denote the following structure.

(2) N. B. Chapman, N. S. Isaacs, and R. E. Parker, *J. Chem. Soc.*, 1925 (1959).

(3) S. O. Greenlee, "Thioxyalkanoic Acids and Epoxy Curing Agents," paper presented to the American Chemical Society Division of Organic Coatings & Plastics Section, Minneaplis, Minn., April 1969.

(4) W. J. Patterson and N. Bilow, *J. Polym. Sci., Part A*, **7**, 1089 (1969).

(5) L. Shechter, J. Wynstra, and R. P. Turkjy, *Ind. Eng. Chem.*, **48**, 94 (1956).

(6) Shechter and J. Wynstra, *ibid.*, **48**, 86 (1956).