chloric acid, and forms a red solution on warming with 2 *N* caustic soda. No other product was isolated.

Anal. Calcd. for $C_{17}H_{13}O_4N_3$: C, 63.15; H, 4.05; N, 13.00. Found: C, 63.20; H, 3.94; N, 13.15.

Infrared Spectra.—Percentage transmission curves, of the compounds suspended in Nujol, were plotted from sample and solvent tracings,[25] obtained with a Perkin–Elmer single beam recording spectrometer (Model-12-A) using a rock salt prism and a 0.025-mm. thick cell.

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[25] We are indebted to Mr. Carl Whiteman for supplying these tracings.

ROCHESTER, N. Y.

[CONTRIBUTION FROM THE MARION EDWARDS PARK LABORATORY OF BRYN MAWR COLLEGE]

The Alkaline Hydrolysis of Ethyl *p*-Alkylbenzoates

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RECEIVED MAY 24, 1952

The rate of the alkaline hydrolysis of ethyl benzoate and of four of its *p*-alkyl derivatives was measured in 85% ethanol and in 56% acetone at 25°. The relative reactivity of the four esters follows a hyperconjugation order in ethanol, but an inductive effect order in acetone.

Almost all of the kinetic work on hyperconjugation has dealt with systems which demand a flow of electrons to the seat of reaction, such as the first-order solvolysis of *p*-alkylbenzhydryl chlorides[2] or aromatic halogenation.[3,4] Since the hyperconjugation effect is believed to be in part a polarizability effect, it will be magnified in the transition state of an electron-demanding process. In reactions which are favored by electron withdrawal, hyperconjugation can only be evident to the extent to which the effect is permanent and not dependent on the special requirements of a reaction.

Indication of the permanency of the hyperconjugation effect has come from the study of certain equilibria, notably the cyanohydrin equilibrium,[5] which are unaffected by polarizability effects and refer to the ground states only. Apart from the equilibria and physico-chemical measurements, as well as scattered investigations resulting in partially inverted series,[6] no kinetic study is reported in which the complete hyperconjugation order was observed in a reaction involving a nucleophilic attack.

The hydrolysis of substituted ethyl benzoates has been studied intensively with regard to substituent effects, and since the mechanism of hydrolysis is reasonably well understood, the reaction can be used to evaluate the unknown effect of substituents. Consequently, the rates of hydrolysis of four ethyl *p*-alkylbenzoates with hydroxide ion were studied at 25° in 85% by weight ethanol and in 56% by weight acetone. The procedures followed those of Evans, Gordon and Watson,[7] and of Tommila and Hinshelwood,[8] respectively. The results are listed in Table I.

TABLE I

RATE CONSTANTS FOR THE ALKALINE HYDROLYSIS OF ETHYL *p*-ALKYLBENZOATES AT 25°

R	H	Me	Et	*i*-Pr	*t*-Bu
(a) In 85% ethanol					
$k_2 \times 10^4$ (l. mole^{-1} sec.$^{-1}$)	6.14 ± 0.08	2.73 ± 0.04	2.93 ± 0.04	3.14 ± 0.05	3.42 ± 0.05
100 k/k_H	100	44	48	51	56
(b) In 56% acetone					
$k_2 \times 10^3$ (l. mole^{-1} sec.$^{-1}$)	2.89 ± 0.03 2.89^a	1.18 ± 0.01 1.14^a 1.21^c	1.06 ± 0.01	0.964 ± 0.004 1.69^b	0.912 ± 0.004 1.02^c
100k/k_H	100	41	37	33	31

^{a} Tommila and Hinshelwood, ref. 8. ^{b} Tommila, *et al.*, ref. 9. ^{c} Price and Lincoln, ref. 10.

The hydrolysis reaction involves a nucleophilic attack as the rate-determining step[11] and is therefore favored by electron-attracting, and suppressed by electron-releasing, groups. In conformity, all alkyl groups should decrease the rate of hydrolysis relative to that of the unsubstituted ester. Whether the order of reactivity within the alkyl groups is *t*-Bu > *i*-Pr > Et > Me or the reverse will depend on whether the permanent hyperconjugation effect or the permanent inductive effect is predominant, *i.e.*, whether the order of electron release is Me > Et > etc., or the reverse. The data in Table I

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[1] British Foreign Scholar and Sir John Dill Fellow of The English Speaking Union. Part of a thesis submitted by Miss M. C. Beckett to the Department of Chemistry of Bryn Mawr College in partial fulfillment of the requirements for the M.A. degree, June, 1951.

[2] E. D. Hughes, C. K. Ingold and N. A. Taher, *J. Chem. Soc.*, 949 (1940).

[3] P. B. D. de la Mare and P. W. Robertson, *ibid.*, 279 (1943).

[4] E. Berliner and F. J. Bondhus, THIS JOURNAL, **68**, 2355 (1946); **70**, 854 (1948); E. Berliner and F. Berliner, *ibid.*, **71**, 1195 (1949).

[5] J. W. Baker and M. L. Hemming, *J. Chem. Soc.*, 191 (1942); see also J. W. Baker, W. S. Nathan and C. W. Shoppee, *ibid.*, 1847 (1935).

[6] V. A. Crawford, *Quarterly Rev.*, **3**, 226 (1949); C. L. Deasy, *Chem. Revs.*, **36**, 145 (1945).

[7] D. P. Evans, J. J. Gordon and H. B. Watson, *J. Chem. Soc.*, 1430 (1937).

[8] E. Tommila and C. N. Hinshelwood, *ibid.*, 1801 (1938).

[9] E. Tommila, L. Brehmer and H. Elo, *Ann. Acad. Sci. Fennicae, Ser.*, **A59**, No. 9, 3 (1942).

[10] C. C. Price and D. C. Lincoln, THIS JOURNAL, **73**, 5836 (1951).

[11] J. N. E. Day and C. K. Ingold, *Trans. Faraday Soc.*, **37**, 686 (1941).

reveal the expected result that the alkyl substituents depress the velocity of reaction in both solvents. In addition, there is evident in 85% ethanol a small but consistent increase from *p*-methyl to *p*-*t*-butyl, the series showing no inversion and increasing in the order Me $<$ Et $<$ *i*-Pr $<$ *t*-Bu $<$ H. The relative magnitudes of the inductive effect predict the reverse of the order obtained. In the obvious absence of steric effects it can be concluded that the permanent hyperconjugation effect is operative. If the magnitude of the over-all polarity of the alkyl groups is considered to be the sum of the two polar effects, one must assume that under the reaction conditions in this particular reaction hyperconjugation is the main contributing factor. In the alkaline hydrolysis of the same five esters in 56% acetone the alkyl groups also retard the reaction relative to the unsubstituted ester, as is expected. But within the alkyl groups the order is the reverse of that obtained in 85% ethanol. The rates of hydrolysis in 56% acetone correspond to an electron release by the alkyl groups in the order *t*-Bu $>$ *i*-Pr $>$ Et $>$ Me. This is clearly the order that would be expected if the predominant polarity were that imposed by the general inductive effect of alkyl groups. As in the hydrolysis in 85% ethanol, the order is well spaced and shows no inversion.

The value of the rate constant for ethyl benzoate in ethanol, found in the present investigation, agrees with that obtained by Evans, Gordon and Watson[7] (6.21×10^{-4}), and the ratio *p*-methyl/H (0.445) with that reported by Ingold and Nathan (0.456).[12] The absolute values differ somewhat, probably because of different conditions and concentrations. At 30° and in 87.83% ethanol Kindler found virtually no difference between the *p*-methyl and the *p*-ethyl compound.[13] However, in the similar hydrolysis of potassium *p*-alkylphenylsulfonates the *p*-ethyl ester reacts faster than the *p*-methyl compound,[14] as was found here. The relative order H $>$ *p*-*t*-Bu $>$ *p*-Me in the hydrolysis of ethyl benzoates in 85% ethanol has also been obtained by Drs. Bevan, Hughes and Ingold.[15] The greater reactivity of the *p*-*t*-butyl compound relative to the *p*-methyl compound has recently been observed in a number of other reactions involving a nucleophilic attack (Table II). While this work was in progress Herbst and Jacox have reported the results of a similar study at 30°, using Kindler's conditions, in which they obtained exactly opposite results.[16] Our data were therefore checked after one-half year by two different investigators, and the earlier results were confirmed. We are unable to explain the discrepancy between our data and those of Herbst and Jacox. These authors report an activation energy of 14.4 kcal. for the alkaline hydrolysis of ethyl benzoate. Values of 17.7 kcal. have independently been reported by two groups of investigators under almost the same conditions (85% ethanol),[7,12] and other reported data, obtained in solvents of slightly different composition, point toward the same value.[17]

In acetone, the rate constants for the unsubstituted and the *p*-methyl compound agree with those reported by Tommila and Hinshelwood,[8] but a somewhat higher value is reported for ethyl *p*-*i*-propylbenzoate.[18] Price and Lincoln have also determined rate constants for the hydrolysis of ethyl *p*-methyl- and *p*-*t*-butylbenzoate in 56% acetone,[10] and they found the same relative order, Me $>$ *p*-*t*-Bu.

The reversal of the relative order of the *p*-alkyl groups, with a change in solvent, must be considered real, in spite of the small absolute differences. How significant this reversal is, cannot yet be decisively answered. Neither of the results could have been predicted with certainty. Both effects of alkyl groups are small; the inductive effect, because of the very smallness of the carbon–hydrogen dipole, and the resonance effect because of the poor overlap of σ-orbitals and the absence of unshared electrons. Therefore, differences in rates, caused by alkyl groups, are also usually very small, and differences in activation energies often within the limits of the experimental uncertainties. Furthermore, polarizability effects are absent or greatly diminished in this reaction, and neither the electron releasing hyperconjugation effect nor the electron releasing inductive effect can be expected to be appreciably magnified in the transition state, beyond what is present in the ground state. The polarizabilities associated with these effects (inductomeric and electromeric) will not develop at the demand of the attacking reagent and will, therefore, not contribute much to the reaction. The resulting differences in rates, which are caused by both effects, represent a very delicate balance of factors, which must be subject to external influences, differing from reaction to reaction and apparently from one solvent to another.[19] This balance can also be upset in electrophilic reactions, as has recently been shown in aromatic nitration of toluene and *t*-butylbenzene, which follows an inductive effect order,[20] contrary to the behavior of these two compounds in bromination and chlorination.[3,4]

In Table II are listed for comparison some relative rates of reactions which depend on an electro-

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(12) C. K. Ingold and W. S. Nathan, *J. Chem. Soc.*, 222 (1936).

(13) K. Kindler, *Ann.*, **450**, 1 (1926); **452**, 90 (1927).

(14) G. N. Burkhardt, C. Horrex and D. I. Jenkins, *J. Chem. Soc.*, 1654 (1936).

(15) Private communication. We are grateful to the authors for their permission to report these unpublished results.

(16) R. L. Herbst, Abstracts of Papers presented at the Meeting of the American Chemical Society, Boston, Mass., April, 1951, p. 44M; R. L. Herbst and M. E. Jacox, THIS JOURNAL, **74**, 3004 (1952).

(17) R. A. Fairclough and C. N. Hinshelwood, *J. Chem. Soc.*, 538 (1937); R. A. Harman, *Trans. Faraday Soc.*, **35**, 1336 (1939); D. P. Evans and H. O. Jenkins, *ibid.*, **36**, 818 (1940).

(18) Reference 9. However, in the hydrolysis of benzyl acetates in acetone, which is also retarded by alkyl groups, the *p*-*i*-propyl ester reacts slower than the *p*-methyl ester (E. Tommila, *Ann. Acad. Sci. Fennicae*, Ser. **A59**, No. 4, 3 (1942) and ref. 8). Some of the physical properties (*i.e.*, d^{20}_{4} and n^{17}_{D}) reported for ethyl *p*-*i*-propylbenzoate (in ref. 9) are at variance with those given by L. Bert, *Bull. soc. chim.*, [4] **37**, 1397 (1925).

(19) To what extent external conditions, such as the nature of the substituting agent, can affect the relative reactivity of alkylbenzenes is shown by the over-all ratio of the rate constants toluene/benzene, which is 465 in bromination (ref. 4), 345 in chlorination (ref. 3), about 23 in nitration (C. K. Ingold, A. Lapworth, E. Rothstein and D. Ward, *J. Chem. Soc.*, 1959 (1931)) and 2.1 in propylation (F. E. Condon, THIS JOURNAL, **70**, 2265 (1948)).

(20) H. Cohn, E. D. Hughes, M. H. Jones and M. G. Peeling, *Nature*, **169**, 291 (1952).

philic attack, in addition to the data on ester hydrolysis and some similar reactions. It is obvious that the spacing is considerably larger in the former case and that the hyperconjugation effect is appreciably more pronounced. Whereas in the former reactions the difference from one alkyl group to another is roughly one-third, in ester hydrolysis the total difference between the *p*-methyl and *p*-*t*-butyl compound is less than 30%. This reduction in the difference reflects the diminution of hyperconjugation because of the absence of any appreciable polarizability effects in a reaction which depends on a nucleophilic attack. The conclusion, first expressed by Baker,[21] that the hyperconjugation effect consists of a polarizability component, which depends on the particular reaction, and a permanent component, residing in the resting molecule, is thus confirmed and strengthened. To this must be added that it is still not possible to predict with certainty which one of the effects will predominate in a given reaction, even in a reaction involving an electrophilic attack, although the investigated cases seem to indicate that the hyperconjugation effect is favored.

TABLE II

Reactions	Relative rates Me	Et	*i*-Pr	*t*-Bu
Electrophilic attack				
First order hydrolysis of *p*-alkylbenzhydryl chlorides[2]	100	75	56	43
Chlorination of alkylbenzenes[3]	100	84	51	32
Bromination of alkylbenzenes[3,4]	100	70	40	18
Nucleophilic attack				
Alkaline hydrolysis of ethyl *p*-alkylbenzoates in ethanol	100	107	115	125
1-Bromo-2-nitro-4-alkylbenzene with piperidine[22]	100	...	...	117
1-Chloro-2,6-dinitro-4-alkylbenzene with sodium ethoxide[23]	100	...	...	176
Neutral hydrolysis of *p*-alkylbenzoic anhydrides[24]	100	...	...	111
Alkaline hydrolysis of ethyl *p*-alkylbenzoates in acetone	100	90	82	77

That both effects are present in the ground state of the molecules has repeatedly been expressed and has recently been reaffirmed.[25] The inductive effect diminishes with the distance in the benzene ring, and should therefore be weakest in the para position.[26] The opposite may be expected from the hyperconjugation effect, which will be strongest over the longer distance.[27] This difference in relative effectiveness of the two factors in the para position may account for the order of reactivity in 85% ethanol, where the hyperconjugation effect determines the order. Why this relative order is reversed in aqueous acetone is a more difficult question. The main difference in conditions between the two sets of reactions is the greater water content in the acetone–water mixture,[28] and the reason for the reversal of the order must be sought in this fact. The solvent has an important effect on activation energies and entropies. The hydrolysis of ethyl benzoate proceeds with over 3 kcal. less activation energy in the more aqueous 56% acetone than in 85% ethanol.[7,8,12] The reduction of activation energy in acetone is due to the greater solvation of the ionic transition state relative to the less solvated ground state. Why this absolute reduction in activation energy should invert the differential order of reactivity caused by the alkyl groups is however not obvious. Price and Lincoln, who have assumed solvation to be the sole cause of the lower rate for the *p*-*t*-butyl compound, have proposed a reduction of solvation for this compound due to a distant steric effect which prevents the solvent molecules and dipoles from proper orientation.[10] There may, however, be changes in the magnitude of the electronic effects of the substituents due to solvent interaction or stabilization. The change of order of substituents with a change of solvent is not confined to the alkyl groups. The alkyl groups are in many respects similar to the halogens in their dual character and shifting balance between inductive and resonance effects. The order of reactivity of the meta halogens in ester hydrolysis is Br > I > Cl > F in 85% ethanol,[29] but Cl > Br > F > I in 56% acetone.[9,30]

The evidence from ester hydrolysis points to the possibility that solvation forces stabilize the polarity brought about by the general inductive effect, perhaps through dipole association. The solvent effect must be connected with the way *relative* dissociation constants of meta and para substituted benzoic acids are affected by the dielectric constant of the solvent, and with the important observation of Wooten and Hammett[31] that substituents which increase the strength of an acid also increase its relative strength, and *vice versa*, on going from water to butanol. In other words, *p*-toluic or *p*-anisic acid are stronger acids in water, relative to benzoic acid, than in butanol, and the reverse is true of *p*-nitrobenzoic acid.[32] On changing from one solvent to another the changes of the effect of a substituent depend also on the substituent, and if the differences are very small, as in the case of alkyl groups, the transi-

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(21) J. W. Baker, *J. Chem. Soc.*, 1150 (1939).

(22) E. Berliner and L. C. Monack, THIS JOURNAL, **74**, 1574 (1952).

(23) C. W. L. Bevan, E. D. Hughes and C. K. Ingold, quoted by J. F. Bunnett and E. Zahler, *Chem. Revs.*, **49**, 273 (1951).

(24) E. Berliner and L. Holljes Altschul, THIS JOURNAL, **74**, 4110 (1952).

(25) N. N. Lichtin and P. D. Bartlett, *ibid.*, **73**, 5530 (1951).

(26) A. Lapworth and R. Robinson, *Mem. Proc. Manchester Lit. and Phil. Soc.*, **72**, 43 (1927); J. D. Roberts, R. A. Clement and J. J. Drysdale, THIS JOURNAL, **73**, 2181 (1951); K. L. Nelson and H. C. Brown, *ibid.*, **73**, 5605 (1951); also ref. 25.

(27) A. E. Remick, "Electronic Interpretations of Organic Chemistry," 2nd Ed., John Wiley and Sons, New York, N. Y., 1949, p. 586.

(28) The dielectric constant of the alcohol–water mixture is about 30, and that of the acetone–water mixture about 46: G. Åkerlöf, THIS JOURNAL, **54**, 4124 (1932); R. A. Fairclough and C. N. Hinshelwood, ref. 17.

(29) K. Kindler, ref. 13 and *Ber.*, **69**, 2792 (1936).

(30) E. Tommila, *Ann. Acad. Sci. Fennicae*, Ser. **A57**, No. 13, 3 (1941).

(31) L. A. Wooten and L. P. Hammett, THIS JOURNAL, **57**, 2289 (1935); see also A. E. Remick, ref. 27, Chapter 8.

(32) This wider spread of values in a non-polar solvent is reflected in the greater rho value for the ionization constants of benzoic acids in alcohol relative to water: L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Company, Inc., New York, N. Y., 1940, Chapter 7; J. D. Roberts, E. A. McElhill and R. Armstrong, THIS JOURNAL, **71**, 2923 (1949).

TABLE III

THE HYDROLYSIS OF ETHYL *p*-ALKYLBENZOATES AT 25°

Time, min.	Ml. NaOH (0.0585 *N*)	x, ml.	$k_2 \times 10^4$, l. m.$^{-1}$ sec.$^{-1}$	Time, min.	Ml. NaOH (0.0585 *N*)	x, ml.	$k_2 \times 10^4$, l. m.$^{-1}$ sec.$^{-}$
[Ethyl *p*-toluate] = $[OH^-]$ = 0.0525 *M* [HCl] = 0.0676 *N*				[Ethyl *p*-*t*-butylbenzoate] = $[OH^-]$ = 0.0580 *M*			
(a) In 85% ethanol							
0	(2.58)	...	...	0	(1.64)	...	...
240	4.15	1.57	2.80	120	2.87	1.23	3.39
420	4.98	2.40	2.76	240	3.87	2.23	3.47
540	5.45	2.87	2.76	360	4.64	3.00	3.46
660	5.84	3.26	2.74	540	5.55	3.91	3.46
780	6.17	3.59	2.71	660	6.01	4.37	3.43
1260	7.20	4.62	2.67	1380	7.73	6.09	3.31
1380	7.42	4.84	2.69	1560	8.03	6.39	3.34
1500	7.62	5.04	2.71	∞	(11.56)	(9.92)	
∞	(11.56)	(8.98)					
[Ethyl *p*-toluate] = $[OH^-]$ = 0.0581 *M* [HCl] = 0.0670 *N*	0.0481 *N* NaOH, ml.			[Ethyl *p*-*i*-propylbenzoate] = $[OH^-]$ = 0.0581 *M*	0.0481 *N* NaOH, ml.		
(b) In 56% acetone							
0	(1.86)	...	...	0	(1.86)	...	...
36	3.44	1.58	1.20	43	3.39	1.53	0.968
76	4.76	2.90	1.19	79	4.37	2.51	.953
119	5.84	3.98	1.19	122	5.35	3.49	.956
161	6.67	4.81	1.18	193	6.61	4.75	.964
203	7.36	5.50	1.18	255	7.43	5.57	.964
265	8.16	6.30	1.18	323	8.15	6.29	.966
325	8.79	6.93	1.19	385	8.64	6.78	.955
384	9.26	7.40	1.18	452	9.15	7.29	.967
∞	(13.93)	(12.07)		∞	(13.93)	(12.07)	

TABLE IV

SUMMARY OF RESULTS

H	Dev.	*p*-Methyl	Dev.	*p*-Ethyl $k_2 \times 10^4$ (l. m.$^{-1}$ sec.$^{-1}$)	Dev.	*p*-*i*-Propyl	Dev	*p*-*t*-Butyl	Dev.
(a) In ethanol									
6.14	0.05	2.75	0.04	2.92	0.03	3.15	0.06	3.40	0.06
6.11	.05	2.69	.04	2.93	.06	3.14	.07	3.41	.05
6.19	.09	2.73	.04	2.93	.02	3.13	.02	3.43	.04
6.13	.11	2.73	.03			3.16	.06	3.45	.04
		2.72	.04	Av. 2.93	± .04	3.14	.05		
Av. 6.14	± .08	2.77	.05	2.95^a	.06			Av. 3.42	± .05
6.20^a	.05	Av. 2.73	± .04	$2.93^{a,b}$	.05	Av. 3.14	± .05	3.42^a	.05
6.18^a	.11					3.16^a	.04	$3.49^{a,b}$	.02
$6.24^{a,b}$	.02	2.73^a	.07			$3.17^{a,b}$	.05	$3.43^{a,b}$	.05
		2.79^a	.04						
		$2.73^{a,b}$	.02						
$k_2 \times 10^3$ (l. m.$^{-1}$ sec.$^{-1}$) (b) In acetone									
2.88	0.03	1.19	0.01	1.07	0.01	0.965	0.002	0.910	0.004
2.91	.03	1.18	.01	1.06	.01	.962	.005	.915	.003
2.89	.04	1.17	.01	1.06	.01	.966	.005	.916	.004
2.91	.02	1.19	.01	Av. 1.06	± .01	Av. .964	± .004	.908	.004
2.88	.02	Av. 1.18	± .01					Av. .912	± .004
Av. 2.89	± .03								

[a] These runs were conducted by E. A. B. and B. N. after a time interval with new solutions. They are not included in the averages. [b] Cresol red was used as the indicator.

tion may well bring about a complete change of order.

Our present knowledge of the relation between a given solvent and the magnitude of electronic effects of substituents is not far enough advanced to offer a satisfactory explanation. But it may well be that conflicting and inverted orders, often obtained in reactions involving alkyl groups, may in part be due to such effects of the solvent.

Experimental

Preparation of Esters (M.C.B.).—All esters were obtained from the acids which had been crystallized to a constant melting point. Benzoic acid and *p*-toluic acid were commercial samples which after several crystallizations from aqueous acetic acid and aqueous ethanol, respectively, melted at 122.6–123.1° and 179.2–179.9° (cor.). The other three acids were prepared by hypobromite oxidation of the respective *p*-alkylacetophenones. Of these, *p*-ethylacetophenone was a commercial product, and the other two were prepared by a method described in the literature.[33] The purified acids had the following melting points (cor.): *p*-ethyl 113.4–113.9° (ligroin), *p*-*i*-propyl 116.7–117.1° (ligroin), *p*-*t*-butyl 165.8–166.2° (aqueous ethanol). A commercial sample of *p*-*i*-propylbenzoic acid softened at 112.7° and melted at 113.4–114.7°, in spite of numerous crystallizations; it was discarded. The pure acids were esterified with an excess of absolute ethanol and sulfuric acid in the usual manner.[34] The twice distilled esters, after rejection of an initial and a final fraction, had the following boiling points and $n^{20}\text{D}$: *p*-H 79–79.5° (2–3 mm.), 1.5048; *p*-methyl 82–83° (2 mm.), 1.5080; *p*-ethyl 73.2–74.2° (1 mm.), 1.5060; *p*-*i*-propyl 89–90° (1.5 mm.), 1.5030; *p*-*t*-butyl 99.5–101° (1 mm.), 1.5020.

Kinetic Procedure (a) In Ethanol[7] (M.C.B.).—The alcohol-water mixture was exactly 85% by weight, as determined from the density (d^{25}_{25} 0.82901). The alcoholic hydrolyzing agent was made by dissolving clean, dry sodium directly in the 85% ethanol (about 250 ml.), properly protected from moisture and carbon dioxide. The concentration was approximately 0.2 *M* so that 25 ml. diluted to 100 ml. was approximately 0.05 *M*. This solution was checked frequently and only small amounts were made up at a time. An amount of ester, equivalent exactly to the number of moles of alcoholic sodium hydroxide in 25 ml., was transferred quantitatively into a 100-ml. volumetric flask by solution in thermostated 85% ethanol (about 70 ml.). A 25-ml. sample of the hydrolyzing solution was pi-

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[33] C. F. H. Allen, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 3.

[34] L. F. Fieser, "Experiments in Organic Chemistry," 2nd Ed., D. C. Heath and Co., Boston, Mass., 1941, p. 62.

petted into the flask, the mixture was made up to volume, well shaken and replaced in the thermostat (25 ± 0.05°). The esters react slowly enough to make this procedure possible. At suitable intervals 10-ml. samples were withdrawn, added to 10 ml. of $N/15$ hydrochloric acid, and the excess acid was back-titrated with $N/20$ sodium hydroxide. In the case of the less soluble esters 10 ml. of alcohol was added before the final titration, in order to keep the organic material in solution. Failure to do so resulted in erratic end-points. The indicator was brom thymol blue (5 drops) and the end-point was matched against the color of 5 drops of indicator in 15 ml. of a $M/30$ sodium benzoate solution and 15 ml. of 50% alcohol. A 10-ml. microburet, graduated in 0.02 ml., was used for all titrations. Rate constants were calculated from the bimolecular equation for equal concentrations. There was a slight downward drift of the rate constants in the early parts of the runs and samples were usually withdrawn between 20 and 70% reaction. In a few runs cresol red was used as an indicator. The end-point was sharper, but an indicator blank had to be applied. The results of two typical determinations are recorded in Table III, and in Table IV are listed the results of all the runs.

(b) **In Acetone**[8] (E.A.B. and B.N.).—A stock solution (3 liters) of aqueous acetone was prepared by diluting 400 ml. (or 800 ml.) of carbonate-free water in a 1-l. (or 2-l.) volumetric flask to volume with purified acetone, both solvents having been thermostated. A density determination showed the stock solution to contain 55.86% by weight acetone. The solution containing the sodium hydroxide for the hydrolysis was prepared daily. Eighty ml. of $N/4$ sodium hydroxide was pipetted into a 200-ml. volumetric flask and diluted to volume with pure acetone. The normality of this solution was frequently checked, and was found to agree with that calculated on the basis of the initial concentration of sodium hydroxide. About 0.05 mole of ester, corresponding exactly to the normality of the sodium hydroxide solution, was transferred quantitatively with the acetone–water solvent to a 100-ml. volumetric flask. Fifty ml. of the 0.1 N sodium hydroxide solution was added, the flask was filled up to volume with aqueous acetone, rapidly shaken and replaced in the thermostat. Zero time was taken as half the delivery time of the sodium hydroxide solution. The sampling was carried out as described above for the runs in alcohol. Five drops of cresol red were used as indicator. Except for the unsubstituted and the *p*-methyl compounds, 10 ml. of acetone was added before titration, because otherwise the organic material precipitated in part during the titration and the end-point was not sharp. The additional acetone did not change the end-point since the same constant was obtained for ethyl *p*-methylbenzoate with and without the addition of acetone. Two typical runs are listed in Table III and the summary of all kinetic runs in Table IV.

Acknowledgment.—The help afforded by a Frederick Gardner Cottrell Grant of the Research Corporation is gratefully acknowledged.

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NOTES

Non-exchange of Oxygen between Water and Some Compounds of Nitrogen[1]

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RECEIVED APRIL 8, 1952

It has been shown[3] that nitrous oxide undergoes only negligible exchange of oxygen atoms with water of initially neutral *p*H. In the present investigation attempts were made to detect oxygen exchange between water and nitrous oxide, water and hyponitrite ion, and water and nitrohydroxylamite ion over a wider range of *p*H.

Two experiments were carried out in which nitrous oxide was shaken with O^{18}-enriched water (1.5% O^{18}) for 40 hours at 22°. In one experiment the water was made strongly alkaline by reaction with sodium metal; the other experiment was carried out in 1.75 N H_2SO_4. After 40 hours no enrichment as large as 0.1% in the O^{18} content of the N_2O was detectable with a Consolidated-Nier "Isotope Ratio" mass spectrometer. From these measurements, a lower limit to the half-time for the exchange of ten years is calculated.

To check further on the relation between N_2O and hyponitrous acid, exchange of oxygen between sodium hyponitrite and water was attempted at various *p*H's. Anhydrous sodium hyponitrite was prepared by the method of Partington and Shah,[4] in which sodium nitrite is reduced by sodium amalgam. The product formed showed all the characteristic chemical properties of hyponitrite; flame photometric analysis of the solid product indicated 41.7% sodium, compared with a calculated value of 43.4%. Appreciable exchange times with water were possible only at relatively high *p*H's in air, since $Na_2N_2O_2$ solutions decompose rapidly *in vacuo* and under any conditions at *p*H 7 or less. Five experiments were carried out in which $Na_2N_2O_2$ was decomposed in 1.5% H_2O^{18} solution at initial *p*H's ranging from 0.05 to 10.6. The longest exchange time in the series was 16 hours at the highest *p*H. In no case was appreciable O^{18} enrichment found in the resultant purified N_2O by mass spectrometric analysis. It is concluded that neither hyponitrous acid nor hyponitrite ion exchanges oxygen atoms with water.

Oxygen exchange was also looked for in the decomposition of aqueous sodium nitrohydroxylamite solutions. $Na_2N_2O_3$ was prepared according to the method reported by Yost and Russell,[5] in which the salt is precipitated from alcoholic solution of sodium ethoxide following the interaction of hydroxylamine and ethyl nitrate. Gravimetric analysis of the product indicated 35.7% sodium, compared with a calculated percentage of 37.6. Aqueous solutions of this compound decompose

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(1) Research carried out under the auspices of the U. S. Atomic Energy Commission.

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