TABLE I

Compound	B.p., °C.	Mm.	n_D	Max. molar heat of mixing with $CHCl_3$	Mole fraction of $CHCl_3$
$Bu_2P(O)OBu$	125–126	1	1.4445^{24}	1430	0.540
$BuP(O)(OBu)_2$	171	26	1.4321^{17}	1380	.542
$PrP(O)(OEt)_2$	102	17	1.4156^{25}	1233	.573
$EtP(O)(OEt)_2$	85–87	16	1.4094^{30}	1155	.570
$(iso\text{-}PrO)_3PO$	99	11	1.4059^{20}	1150	.585
$(PrO)_3PO$	84–86	1	1.4160^{17}	1125	.566
$(BuO)_3PO$	140	2	1.4233^{17}	1122	.615
$(EtO)_3PO$	112	22	1.4060^{17}	1065	.575
$(BuO)_2POH$	131	18	1.4052^{23}	980	.628
$(EtO)_2POH$	82	19	1.4051^{25}	838	.566
$(BuO)_2P(O)Cl$	109	4	1.4302^{23}	709	.605
$(BuO)_3P$	130	17	1.4302^{24}	680	.560
$(EtO)_2P(O)Cl$	54	1	1.4156^{24}	653	.599
$BuOP(O)Cl_2$	92–93	16	.....	440	.534
$EtOP(O)Cl_2$	66–67	15	.....	373	.525
$POCl_3$	105	740	.....	368	.574

It was impossible, unfortunately, to complete the entire series of possible structural variations by inclusion of trialkylphosphine oxides and trialkylphosphines in our study. The former substances are solids, while the latter have such obnoxious physical characteristics that close work with them in the currently used apparatus was effectively precluded. Therefore, it was impossible to establish conclusively whether or not the site of the hydrogen bond formation is a singular atom. The possibility of some bonding at the ester oxygen atoms, at the halogen atoms, and at the phosphorus atom (in the phosphites) still exists. Such multiple sites for hydrogen bonding would tend to cause a shift of the relative concentration of the components toward the chloroform side at the point of maximum heat evolution.[1] Conceivably, however, possible is a factor which may have a simultaneous but opposite effect on the location of the maximum. All systems studied here have rather low degree of stability; they are readily separated into components by simple distillation. As such they may be expected to obey the law of mass action, with substances having the greater heat of mixing with chloroform requiring a lesser preponderance of the latter in the mixture to display the heat maximum. Since all substances studied here have several potential bonding sites, the magnitude of this effect cannot be estimated, with the first effect apparently taking the predominant role.

Among the practical significant points resulting from this study the apparently superior characteristics of the esters of phosphinic and phosphonic acids may be pointed out. While many other factors are involved in the action of plasticizers, the hydrogen bonding effect is one of the more important ones and in this respect compounds of types $RP(O)(OR)_2$ and $R_2P(O)OR$ stand somewhat above trialkyl phosphates.

Experimental Part

The apparatus used was constructed along the lines that were used previously.[1,2] The mixing chamber and the associated equipment were mounted as a unit on the cover of the calorimeter in order to facilitate the removal of this portion of the apparatus for recharging between runs. A glass stirrer was used within the mixing chamber instead of the silver wire,[1] in order to reduce heat exchange with the surroundings.

The substances used in the study were prepared by conventional methods and their constants are given in Table I. One new compound, butyl dibutylphosphinate, was prepared as follows.

A solution of 5.65 g. of sodium in 100 ml. of *n*-butanol was treated with 48.3 g. of dibutylphosphinyl chloride (prepared according to Kosolapoff and Watson[3]), with stirring and ice-cooling. The mixture was diluted with 200 ml. of dry benzene and was allowed to stand overnight. After filtration, there was obtained 35.8 g. (62.4%) of butyl dibutylphosphinate, a colorless liquid, b.p. 125–126° at 1 mm., $n^{24}D$ 1.4445, d^{24}_4 0.9271. Found: *MR*, 67.20; P, 13.32. Calcd. for $Bu_2P(O)OBu$: *MR*, 67.33; P, 13.22.

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[3] Kosolapoff and Watson, THIS JOURNAL, **73**, 4101 (1951).

AUBURN, ALABAMA RECEIVED MAY 28, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF THE UNIVERSITY OF PENNSYLVANIA]

Effect of Structure on Reactivity.[1] IV. Aminolysis of Esters with Secondary Amines

BY EDWARD McC. ARNETT,[2] JOHN G. MILLER AND ALLAN R. DAY

In the aminolysis of esters, secondary amines have been found to be very unreactive relative to primary amines. A number of secondary amines have been studied in the aminolysis of methyl lactate and phenyl acetate both in the presence and absence of ethylene glycol. The relative reactivities are: dimethylamine > piperidine > morpholine > diethanolamine > diethylamine > di-*n*-butylamine > di-*n*-propylamine.

Previous papers[3] in this series have dealt with the ammonolysis and aminolysis, using primary amines, of esters. The present paper reports the use of secondary amines for the aminolysis of esters.

The results show clearly that secondary amines are much less reactive than most primary amines. It was also noted that ethylene glycol which acts as a catalyst for the ammonolysis and primary aminolysis of esters actually hinders the reaction, in certain cases, when secondary amines are used.

Experimental

The experimental method was modified slightly from that of the preceding papers in the series. To increase the accuracy with which the reaction systems were prepared, the ester was delivered to the reaction system by means of a buret before final dilution was made. The densities of the esters and the catalysts were determined immediately before

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[1] From a thesis submitted in April, 1949, by Edward McC. Arnett to the University of Pennsylvania.

[2] du Pont Fellow 1948–1949. Present address: Max Levy and Company, Wayne Avenue and Berkeley Street, Philadelphia, Pa.

[3] (a) M. Gordon, J. G. Miller and A. R. Day, THIS JOURNAL, **70**, 1946 (1948); (b) M. Gordon, J. G. Miller and A. R. Day, *ibid.*, **71**, 1245 (1949); (c) E. McC. Arnett, J. G. Miller and A. R. Day, *ibid.*, **72**, 5635 (1950).

TABLE I

REACTION RATES OF VARIOUS AMINES WITH PHENYL ACETATE IN THE PRESENCE AND ABSENCE OF ETHYLENE GLYCOL

Amine	Velocity constant No glycol	Velocity constant Glycol present	pK_a
Piperidine	Immeasurably rapid	Immeasurably rapid[a]	11.06[b]
Ethylamine	....	Immeasurably rapid	10.67
Dimethylamine	Immeasurably rapid	Immeasurably slow	10.71
Morpholine	$3.39 (\pm 0.13) \times 10^{-1}$	2.73×10^{-1} (h.l.r.)	8.74[c]
Isopropylamine	$5.31 (\pm 0.98) \times 10^{-2}$	8.51×10^{-4} (h.l.r.)	10.63
Diethylamine	2.80×10^{-3} (h.l.r.)	Immeasurably slow	10.98
Di-*n*-butylamine	$11.00 (\pm 2.00) \times 10^{-4}$	Immeasurably slow	11.31
Di-*n*-propylamine	$9.40 (\pm 1.60) \times 10^{-4}$	Immeasurably slow	10.91
Diethanolamine	Immiscible	3.10×10^{-2} (h.l.r.)	8.88

[a] Goes immediately to 70–80% aminolysis and then stops completely. Repeated three times. [b] Calculated from the work of W. F. K. Wynne-Jones and G. Salamon, *Trans. Faraday Soc.*, **34**, 1321 (1938). [c] Calculated from the work of A. R. Ingram and W. F. Luder, THIS JOURNAL, **64**, 3043 (1942).

they were measured out by volume. The Meeker–Wagner boric acid method[4] was used for the titration of the amines. A model G Beckman *p*H meter was used to determine the equivalent point in the titrations because the use of indicators was precluded by the colorations that developed with most of the secondary amines.

The following compounds were used: phenyl acetate, b.p. 78° at 10 mm., n_D 1.5033 at 20°; methyl lactate, 50° at 17 mm., 1.4140 at 20°; dimethylamine, 7.4° at 760 mm.; diethylamine, 55.5° at 759 mm., 1.3873 at 17.6°; di-*n*-propylamine, 110.7° at 760 mm., 1.4046 at 19.5°; di-*n*-butylamine, 159° at 761 mm., 1.4175 at 20°; diethanolamine, 125° at 1 mm., 1.4776 at 20°; morpholine, 126° at 760 mm., 1.4523 at 25°; and piperidine, 106° at 760 mm., 1.4534 at 20°. The physical constants, purification and methods of handling the other compounds used have been described in the preceding paper.[3c]

Methyl lactate showed definite hydrolysis during the titration procedure. Error due to this was minimized by rapid titration. The phenyl acetate showed no appreciable tendency to hydrolyze under the conditions used.

Results

Due to the low reactivity of the secondary amines, it was not possible to study most of them with methyl acetate which had been used throughout the work with the primary amines. Methyl lactate and phenyl acetate were used and a sufficient number of both primary and secondary amines were studied with these and methyl acetate to permit the comparisons desired.

Unless otherwise specified, the ester concentration was 1 molar and the amine concentration approximately 2 molar. The bimolecular rate constants are expressed in l. mole^{-1} hour^{-1}. All measurements were carried out at 25 ± 0.02° with dioxane as diluent solvent.

The only secondary amines studied with methyl acetate were morpholine, diethylamine and di-*n*-butylamine. Only morpholine was studied in the absence of a catalyst and it showed no measurable reaction. In the presence of 5 moles of ethylene glycol per liter, a *k* value of $9.05 (\pm 0.62) \times 10^{-5}$ was found for morpholine, the other two reacted immeasurably slowly.

Table I lists the velocity constants for the reactions of a group of secondary and two primary amines with phenyl acetate both in the absence of a catalyst and with 5 moles of ethylene glycol per liter present as catalyst. In some cases the velocity constants for the secondary amines showed so much drift that an average velocity constant could not be computed. In such instances, the values listed are the *k* values for the half-life time. These half-life rates are designated by the abbreviation h.l.r., while the standard deviations are noted for those constants which showed no appreciable drift. The aqueous pK_a values are included for later discussion.

A similar set of experiments using methyl lactate as the ester is reported in Table II.

TABLE II

REACTION RATES OF VARIOUS AMINES WITH METHYL LACTATE IN THE PRESENCE AND ABSENCE OF ETHYLENE GLYCOL

Amine	Velocity constant No glycol	Velocity constant Glycol present[a]
Ethylamine	....	Immeasurably rapid
Dimethylamine	9.80×10^{-4} (h.l.r.)	$8.47 (\pm 0.18) \times 10^{-4}$
Piperidine	$3.15 (\pm 0.12) \times 10^{-4}$	$1.81 (\pm 0.04) \times 10^{-3}$
Morpholine[b]	1.06×10^{-4}	$2.42 (\pm 0.16) \times 10^{-4}$
Diethylamine	Immeasurably slow	Immeasurably slow

[a] Ethylene glycol concentration 5 molar. [b] Ester concentration 0.734 molar.

Discussion

In the investigation of the primary amines, the use of methyl acetate as the ester throughout permitted a simple comparison of the steric effects due to the amines. The use of more than one ester on the study of the secondary amines obviously superimposes the relative steric effects of the esters on those of the amines. Accompanying this complication there appeared a steric effect of the ester on the catalysis of the reaction. This is apparent from the data in Table I. In every case where comparable rates could be measured, phenyl acetate reacted more rapidly in the absence of ethylene glycol than in its presence. It has been thoroughly demonstrated that ethylene glycol is a strong catalyst in the aminolysis of other esters.[3] It has also been shown that phenyl acetate is a very reactive ester[3a,b] compared to the other acetates in ammonolysis. The lowered reactivity in the presence of ethylene glycol is in all probability due to the bulk of the complexes formed by hydrogen bonding between the amines and the glycol. Evidently, due to the size of the benzene ring and the coplanarity of the carbonyl grouping with the benzene ring caused by resonance, this ester presents a much smaller passageway than does methyl acetate for the approach of the nitrogen atom of the amine to the carbon atom. Ammonolytic rates indicated that this

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[4] E. W. Meeker and E. C. Wagner, *Ind. Eng. Chem., Anal. Ed.*, **5**, 396 (1933).

passageway was not large enough to admit the additional group in the case of the naphthyl acetates.[3a]

With such a narrowed entrance the complexes of glycol and amine cannot easily reach the carbonyl carbon atom. Although the free amine molecules might gain access to the cationoid carbon, their number would be reduced to a value lower than in the absence of the glycol and for that reason we should expect a lowering of the rate by the glycol.

Further evidence for the steric factor can be seen from the order of amines in Table I. Piperidine and morpholine, in which hindrance is relieved by the folding back of the carbon chains by ring formation, have the greatest reaction rates of the secondary amines and in the case of morpholine the rates with and without glycol are nearly the same. As we pass down the series not only does the rate steadily diminish as the predicted steric hindrance increases, but we see also a general trend for a larger difference between the rates with and without ethylene glycol as a result of superimposing steric effects of amine and glycol.

Methyl lactate lies between methyl acetate and phenyl acetate in reactivity, to judge from the results obtained with morpholine. The relative activity of this ester in ammonolysis has been discussed in a previous paper.[3a] In every case shown in Table II, methyl lactate, although less reactive than phenyl acetate, shows catalysis by ethylene glycol, attesting to its freedom from steric hindrance.

The secondary amines are very much less reactive than primary amines. The attachment of the second alkyl group increases the screening of the nitrogen atom so greatly that the slight contribution to reactivity caused by augmenting the charge on the nitrogen is completely overshadowed. In general, basicity in this series has little effect on the order of activity unless the steric factors are practically identical for the amines being discussed. Such is the case with piperidine and morpholine and it will be noted that the more basic piperidine reacts much more rapidly.

Dimethylamine is the most reactive of the secondary amines studied. The only exception is its failure to react with phenyl acetate in the presence of ethylene glycol. This must mean that in the hydrogen-bonded complex which the amine forms with ethylene glycol the nitrogen atom must be effectively screened. Piperidine is a relatively basic amine and relatively unhindered. Morpholine is less basic than piperidine and also less reactive. Diethylamine, although slightly more basic than dimethylamine, is far less reactive as a result of increased steric hindrance. The severity of the steric restrictions is reflected in the failure to react with methyl lactate which is relatively unhindered. The order of the next three secondary amines, $(C_2H_5)_2NH > (n\text{-}C_4H_9)_2NH > (n\text{-}C_3H_7)_2NH$, suggests that a "delta effect"[3c] may be operative in the case of di-*n*-butylamine. Unfortunately, the precision of the measurements is insufficient to establish the existence of the effect in this case. The fact that the basicity constants are in the order di-*n*-butyl > diethyl > di-*n*-propyl, suggests that the delta effect may be more marked where the hydronium ion is the reference acid. The reactivity of diethanolamine is assumed to be due to hydrogen bonding between the hydroxyl groups, which would be expected to bend the carbon chains away from the nitrogen atom and thus reduce steric hindrance.

PHILADELPHIA, PENNA. RECEIVED MARCH 28, 1951

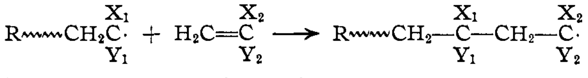
[CONTRIBUTION NO. 111 FROM THE GENERAL LABORATORIES OF THE UNITED STATES RUBBER COMPANY]

Rate Constants in Free Radical Polymerizations. IV. Methyl Acrylate[1]

BY MAX S. MATHESON,[2] E. E. AUER, ELLEN B. BEVILACQUA AND E. J. HART

The propagation and termination rate constants for methyl acrylate polymerization have been measured by the rotating sector method. With this monomer, under our experimental conditions, the increasing viscosity of the system causes chain termination to become diffusion-controlled even in the initial stages of polymerization. As a result, the rate of polymerization accelerates essentially at the beginning of the reaction. The rate constants for methyl acrylate have been compared with the results of Melville and Bickel on butyl acrylate, and also with the data previously obtained on methyl methacrylate, vinyl acetate and styrene. The comparison shows that, for vinyl polymerization, the frequency factors in chain propagation are low but in chain termination are nearly normal, and that the activation energies for propagation are 6–8 kilocalories, while the values for the termination reaction are somewhat lower, but not zero.

The study of polymerization rate constants yields an insight into the effects of structure on the reactivity of olefinic compounds (monomers) or of the derived radicals. From copolymerization studies one may obtain the ratio of the rate constants for the addition of two monomers to the same radical in the propagation reaction shown



$$R\!\sim\!\sim\!\sim CH_2\underset{Y_1}{\overset{X_1}{C}}\cdot + H_2C{=}\underset{Y_2}{\overset{X_2}{C}} \longrightarrow R\!\sim\!\sim\!\sim CH_2{-}\underset{Y_1}{\overset{X_1}{C}}{-}CH_2{-}\underset{Y_2}{\overset{X_2}{C}}\cdot$$

Such ratios have shown how monomer reactivity toward a given radical depends on the nature of the substituent groups X_2 and Y_2.[3,4] However, reactivities of different radicals toward a given monomer can only be deduced when the individual propagation rate constants are known. In recent years such absolute values have been obtained on several monomers, vinyl acetate,[5,6,7] methyl meth-

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(1) This work was carried out with the assistance of the Office of Naval Research under Contract N8 onr-544.

(2) Argonne National Laboratory, Chicago, Illinois.

(3) F. R. Mayo, F. M. Lewis and C. Walling, THIS JOURNAL, **70**, 1529 (1948).

(4) F. R. Mayo and C. Walling, *Chem. Revs.*, **46**, 191 (1950).

(5) (a) G. M. Burnett and H. W. Melville, *Nature*, **156**, 661 (1945); (b) *Proc. Roy. Soc.* (*London*), **A189**, 456 (1947).

(6) (a) P. D. Bartlett and C. G. Swain, THIS JOURNAL, **67**, 2273 (1945); (b) C. G. Swain and P. D. Bartlett, *ibid.*, **68**, 2381 (1946); (c) H. Kwart and P. D. Bartlett, *ibid.*, **72**, 1060 (1950).

(7) M. S. Matheson, E. E. Auer, E. B. Bevilacqua and E. J. Hart, *ibid.*, **71**, 2610 (1949).