way as Table I, but for $K(0) = 3.50 \times 10^{-4}$ and $c = 1.025 \times 10^{-4}$ molar. The data for the last column of Table I lie very close to curve C. Thus a difference of this order in $K(0)$ gives rise to a difference in $\Delta\lambda/\lambda_0$ (%) of one unit. This procedure therefore constitutes a sensitive method for estimation of $K(0)$.

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Exchange Reactions of Methane and Monodeuteromethane with Atomic Deuterium

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The reaction of atomic deuterium, produced by the discharge-tube method, with methane has been investigated a number of times.[1] The reaction takes place at an appreciable rate only at elevated temperatures, as it appears to have both a relatively high activation energy and a relatively low steric factor.[2] As yet, no unequivocal choice of mechanism for the exchange has been possible. The suggestions are (a) hydrogen abstraction, $D + CH_4 = CH_3 + HD$, followed by exchange of the methyl radical prior to stabilization as a deuteromethane, and (b) an inversion process, $D + CH_4 = CH_3 + H$. Since CH_3 radicals are known to exchange rapidly with D atoms,[3] in excess of the latter mechanism (a) would lead to CD_4 as the major exchange product. With mechanism (b) operative, the major product would be CH_3D. In the present work, the distribution of product deuteromethanes from the $D + CH_4$ reaction has been determined by means of mass spectrometry. CD_4 was found to constitute about 80% of the exchange product, most of the remaining deuteromethane being CHD_3. Strong evidence is thus provided that mechanism (a) alone accounts for this exchange.

In an extension of this work, the analogous $D + CH_3D$ reaction was investigated with a view to determining the nature of possible isotope effects. In terms of mechanism (a), the rate-determining reactions to be considered are

$D + CH_4 = CH_3 + HD$ (rate constant $= 4k_1$)
$D + CH_3D = CH_2D + HD$ (rate constant $= 3k_2$)
$D + CH_3D = CH_3 + D_2$ (rate constant $= k_3$)

k_2 and k_3 should differ in magnitude due to zero-point energy differences. Taking the values of the C–H and C–D stretching frequencies in CH_3D to be 3000 and 2200 cm.$^{-1}$,[4] one can readily estimate the rate constant ratio $k_3/k_2 = 0.40$ at 350°.[5] Whence, if k_1 and k_2 are assumed identical, the relative rates of exchange of CH_3D and CH_4 should be $(3k_2 + k_3)/4k_1 = 0.85$. In the present study, known mixtures of CH_3D and CH_4 were exchanged with atomic deuterium, and it was found that the CH_3D/CH_4 ratio did not change within the experimental error during 50% reaction. Since it is inconceivable that k_2 and k_3 be identical, it appears that k_2 must in fact be greater than k_1. Support for this hypothesis comes from the data on electron-impact bond-breakage probabilities for C–H in CH_4, C–H in CH_3D and C–D in CH_3D. A ratio of 1.00:1.21:0.46 is obtained if one averages the results of the several studies reported.[6] If the D-atom exchange rate constants bear the same type of relationship to one another, nearly identical rates of exchange for CH_4 and CH_3D are to be expected, since in this event $(3k_2 + k_3)/4k_1 = 1.02$.

Experimental

The exchanges were effected in a conventional Wood tube type of apparatus,[7] utilizing a water-jacketed discharge-tube and a 2.5 liter spherical reactor flask. The reactor was enclosed by an electrically-heated transite oven, and its temperature controlled manually, temperature readings being taken on three strategically placed thermocouples on the walls of the bulb. Atom concentrations, which ranged between 10 and 20% in the various experiments, were estimated by means of a Wrede–Harteck gage. The glass surface of the reactor was "poisoned" toward hydrogen atom recombination by a coating of pyrophosphoric acid, which proved quite effective even at the elevated temperatures of the experiments. The methane reactant was introduced into the center of the reaction vessel at a rate of about 1 cc. per minute at N.T.P. At the low pressure within the reactor (0.5 mm.) rapid diffusional mixing with the excess of partially dissociated deuterium took place (rate of deuterium flow was 65 cc. per minute at N.T.P.). On leaving the reactor, the methane products and a small amount of deuterium were retained in a silica gel trap maintained at liquid air temperature. At the completion of the run, usually of 10 to 15 minutes duration, the methanes were separated from the adsorbed deuterium by repeated distillation between two alternately chilled silica gel traps. The methanes were then completely desorbed by warming to −80° and samples taken for mass spectrometric assay.

Pure methane was prepared by the hydrolysis of methylmagnesium iodide in an atmosphere of hydrogen. The Grignard was prepared as a paste in dioxane, and aqueous dioxane added as hydrolyzing reagent. The gas was purified by passage through traps at Dry Ice and liquid air temperatures, and finally condensed into a pumped-down liquid-oxygen-cooled trap at −215°. Monodeuteromethane of high purity was similarly prepared, using rigorously dehydrated solvent and 99.97% heavy water. The methane/deuteromethane mixtures for use in the isotope effect experiments were made up manometrically. Deuterium was produced by the electrolysis of 99.97% heavy water containing a little NaOD. Small samples of CH_2D_2 and CHD_3 were prepared for mass spectrometer calibration purposes by the action of aluminum/mercury couple on CH_2I_2 and $CHBr_3$, respectively, in the presence of 99.97% heavy water.

The mass spectrometric analyses were performed on a Consolidated Engineering Corporation mass spectrometer. Calibration spectra of CH_4, CH_3D, CH_2D_2 and CHD_3 were obtained from samples of these gases as prepared above, while that of CD_4 was calculated from the spectrum of CH_4, to which it is closely enough analogous for our purpose.[6b,c] The parent peak sensitivities of the various methanes were assumed identical in making the composition computations. The percentages quoted for CH_4, CH_3D, CHD_3 and CD_4 are probably accurate to within one unit, but there is more uncertainty concerning the CH_2D_2 due to the large overlap of

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[7] Reference (1), p. 33–36.

peaks and the fact that it was present in only small amount if at all. There could have been as much as 3% of this constituent without a clear indication of its presence.

The results obtained are tabulated below. The evidence for near-complete exchange is clear in every instance. Experiments 7 and 8 show unmistakably that there is no appreciable difference in the rates of CH_4 and CH_3D exchange.

Expt. no.	2	3	4	5	6	7	8
Temp., °C.	360	340	342	365	370	350	350
Reactant methanes, %							
CH_4	100	100	100	0	0	50	33
CH_3D	0	0	0	100	100	50	67
Product methanes, %							
CH_4	39	50	52	0	0	26	16
CH_3D	3	3	2	53	53	25	34
CH_2D_2	0	0	0	0	0	0	0
CHD_3	8	6	4	8	7	11	10
CD_4	50	41	42	39	40	38	40

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A Kinetic Study of the Perkin Condensation[1]

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Base-catalyzed, aldol-type condensations of carbonyl compounds with weak secondary acids capable of losing a proton have been studied to some extent from the standpoint of kinetics and mechanisms.[2] No kinetic studies have been made on the Perkin condensation, but its mechanism has been formulated as an aldol-type condensation of an acid anhydride with an aromatic aldehyde.[2a]

The present investigation is concerned with the kinetics of the base-catalyzed condensation of benzaldehyde with phenylacetic acid in acetic anhydride. This particular condensation is of interest as a starting point in the study of the effect of substituents on the benzene ring of both the benzaldehyde and the phenylacetic acid.

Experimental

Reagents.—Commercial benzaldehyde was washed with 10% aqueous sodium carbonate and then with water. It was dried over magnesium sulfate and distilled at reduced pressure (below 30 mm.) in the presence of a little hydroquinone. The acetic anhydride was distilled at 745 mm., and the fraction boiling 137–139° was used. Both of these reagents were purified in small quantities and were used as soon as possible.

The anhydrous amines were obtained from Sharples Chemicals, Inc. The phenylacetic acid was a recrystallized commercial preparation of m.p. 76–77°.

Product Isolation.—The condensation of 54.6 g. of phenylacetic acid and 42.4 g. of benzaldehyde in 80 ml. of acetic anhydride containing 40 ml. of triethylamine was carried out as described before.[3] From the reaction mixture was isolated 60–67 g. (67–75%) of crude α-phenylcinnamic acid of m.p. around 156°. From this crude product 48–52 g. (54–58%) of product of m.p. 172–173° could be obtained by crystallization from 50% ethyl alcohol.

In a similar experiment carried out at room temperature for six days a 63% yield of crude product was obtained.

Kinetic Measurements.—The reactions were carried out in an all-glass apparatus consisting of a 500-ml. three-necked flask fitted with a long air condenser, protected from atmospheric water vapor, and a True-Bore glass stirrer. The reaction flask was immersed in a thermostatically controlled oil-bath whose heating element was contained in the wall of the bath. The temperature was kept constant to within 0.1° at the temperatures used. Varying amounts of phenylacetic acid in 150 ml. of acetic anhydride were added to the reaction flask and allowed to remain in the bath overnight. The benzaldehyde and the amine catalyst were then added with stirring. An initial 5-ml. sample was withdrawn into a pipet fitted with a hypodermic syringe as soon as the mixture was homogeneous. Further samples were taken at regular intervals of time thereafter. The analysis for benzaldehyde was carried out by a modification of the procedure described for the determination of carbonyl compounds in the presence of carboxylic acids.[4] A 5-ml. sample was added to 100 ml. of 90% aqueous methanol and the mixture was allowed to stand for 15 minutes so that the anhydride would be destroyed. The *p*H of the solution was then adjusted to 2.5 with 0.5 *N* aqueous hydrochloric acid and 25 ml. of the 0.5 *N* hydroxylamine hydrochloride in 80% ethyl alcohol (*p*H 2.5) was then added. After a reaction period of 15 minutes the hydrochloric acid formed was titrated with 0.463 *N* carbonate-free sodium hydroxide in 80% methanol to an end-point of *p*H 2.5. The results of the titration of the initial samples coupled with the initial mole ratios of the reagents added were used to calculate the initial concentrations of the runs. Satisfactory agreement within experimental error was obtained in a number of duplicate determinations. The runs with variations in concentrations, catalyst and temperature are summarized in Table I.

TABLE I

SUMMARY OF BASE CATALYZED CONDENSATIONS OF PHENYLACETIC ACID WITH BENZALDEHYDE IN ACETIC ANHYDRIDE AT 100°

Run	Concentrations of reagents, *M* PhCHO	$PhCH_2COOH$	Et_3N	$k \times 10^5$
1	1.058	1.058	0.000	. . .
2	1.002	1.002	.577	7.6
3	0.972	1.944	.560	6.2
4	1.889	0.964	.550	5.7
5	1.032	1.032	.297	7.5
6	1.007	1.007	.580[a]	6.9
7	0.978	0.978	.564[b]	5.9
8	1.076	1.076	.620[c]	5.1
9	1.198	1.198[d]	.690	0.18
10	1.261	0.000	.000	. . .
11	1.256	0.000	.723	0.15
12[e]	1.060	1.060	.611	1.04
13[f]	1.001	1.001	.577	6.3
14[g]	1.014	1.014	.584	10.2

[a] Tri-*n*-propylamine was used as a catalyst. [b] Tri-*n*-butylamine was used as a catalyst. [c] Potassium acetate was used as a catalyst. [d] Acetic acid was added in place of phenylacetic acid. [e] The reaction was carried out at 26°. [f] The reaction was carried out at 80°. [g] The reaction was carried out at 120°.

Results and Discussion

The various runs carried out and their results are summarized in Table I. Typical titration data for

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[1] From the Ph.D. thesis of Keith G. Bremer. Presented before the Division of Organic Chemistry of the American Chemical Society, Atlantic City, N. J., September, 1952.

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