$=CH—C_9H_{19}$), 3 to 4.3 (*m*, 4 1/3, $—CH_2—O—CH_2—$, $=CHCl$ of trans), 4.7 (*q*, 2/3, $=CHCl$ of cis). Mass spectrum (*m/e*) : 246 (*P*), 180 (*P*—HCl—HCHO).

COMPOUND VII. According to a procedure described (*3*), a mixture of 270 grams of acetic acid, 45 grams of sulfuric acid, and 81 grams of paraformaldehyde was heated to 100° to dissolve the aldehyde, cooled to 40°, and added gradually to 95 grams of 1-hexene. After stirring for 21 hours at 55°, the mixture was worked up by distillation to give VII, b.p. 56 to 58° (0.6 mm.), 89 grams (45%). Infrared (cm.$^{-1}$) : 1241 (*S*) and 1730 (*S*) (acetate group), 1085 to 1160 (*S*) (cyclic ether). Mass spectrum (*m/e*) : 186 (*P*), 143 ($P—C_3H_7$), 126 (*P*—HOAc), 96 (*P*—HOAc—HCHO).

COMPOUND VIII. The acetate, VII, 63 grams, was heated under reflux for 6 hours in a mixture of 60 grams of KOH, 100 ml. of water, and 250 ml. of ethanol. Distillation afforded 39 grams (81%) of VIII, b.p. 63 to 65° (2 mm.), n_D^{20} 1.4623. Infrared (cm.$^{-1}$) : 3500 (*S*), 3570 (*S*) (—OH), 1050 to 1160 (*S*) (cyclic ether). NMR (δ): 0.95, 1.28, 1.6 (*m,m,m*, 10, $=CH—C_3H_7$ and $—CH_2—CHOH$), 2.7 to 4.12 (*m*, 5 1/2, $—CH_2—O—CH_2—$, $=CHOH$ of trans), 4.3 (*q*, 1/2, $=CHOH$ of cis). Mass spectrum (*m/e*) : 144 (*P*), 101 ($P—C_3H_7$), 96 ($P—H_2O—HCHO$).

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Kinetics of Methanolysis of Benzoyl Chloride in Methanol-Dioxane Mixtures

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The rates of methanolysis of benzoyl chloride have been determined conductometrically for the reaction in mixtures of methanol and p-dioxane containing 50 to 100 weight % methanol. The first-order rate constants and activation parameters for the reaction in each solvent mixture are reported.

THE HYDROLYSIS and ethanolysis of acid chlorides, particularly benzoyl chloride and substituted benzoyl chlorides, have been the subject of a large number of investigations (*4*). The analogous reaction in methanol and mixed solvents containing methanol have received relatively little attention (*5, 7*). Because of the considerable interest in obtaining sufficient data to formulate a generally acceptable mechanism of solvolysis of acid chlorides and in understanding the nature of the solvent effect in these reactions, the results of a limited investigation of the methanolysis of benzoyl chloride in MeOH-*p*-dioxane mixtures are reported.

Table I gives illustrative data for each composition at one temperature. The expected error in the conductivity, κ, is of the order of 1%.

Table II lists the pseudo-first-order rate constants for three mixed solvents and pure methanol at three temperatures. The values listed are the mean of two to four runs at each composition and temperature. For convenience, the dielectric constant (*3*) for the mixtures at 25° C. is listed. Table III contains the activation parameters derived for the reactions, the entropies having been calculated using the first-order rate constants.

Plots of log k_1 *vs.* log $[CH_3OH]$ show slight but definite curvature, the slope increasing from ~1.1 in the range 52 to 66% MeOH to 1.65 at 81 to 100% MeOH at each temperature.

The observed increase in k_1 at 25° C. with increasing methanol content of the solvent mixture does not correlate linearly with the functions of dielectric constant suggested by either the Laidler and Eyring equation or that of Amis (*1*).

EXPERIMENTAL

Chemicals. Fisher reagent grade methanol was dried by refluxing over magnesium oxide, then fractionated in a 50-cm. column packed with glass helices. The fraction collected at 63.90–4.05° C./741 mm. had a refractive index, n_D^{22}, of 1.3282.

Fisher reagent grade benzoyl chloride was distilled through an ordinary fractionating head; the middle portion recovered at 195.0–7.2° C./740 mm. had $n_D^{22} = 1.5525$.

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Table I. Illustrative Runs in Methanolysis of Benzoyl Chloride

Solvent. 52 Wt.% Methanol, 48 Wt. % Dioxane, 35° C.

t, Sec.	$10^4\kappa$, Ohm^{-1} Cm.$^{-1}$
0	0
25	0.427
39	0.656
47	0.764
56	0.888
62	0.970
73	1.08
83	1.21
92	1.26
101	1.37
110	1.45
119	1.57
130	1.62
⋮	
2400	$3.26 = \kappa_\infty$

Solvent. 66 Wt. % Methanol, 34 Wt. % Dioxane, 30° C.

	$10^5\kappa$, Ohm^{-1} Cm.$^{-1}$
0	0
30	1.92
42	2.65
51	3.30
64	4.06
74	4.53
80	4.88
87	5.25
95	5.68
104	6.00
114	6.60
120	6.77
130	7.29
137	7.50
145	7.93
154	8.30
⋮	
3000	$19.7 = \kappa_\infty$

Solvent. 81 Wt. % Methanol, 19 Wt. % Dioxane, 24° C.

	$10^4\kappa$, Ohm^{-1} Cm.$^{-1}$
0	0
30	0.342
44	0.463
54	0.550
63	0.636
72	0.721
83	0.799
91	0.900
100	0.963
111	1.04
120	1.10
151	1.33
160	1.39
169	1.43
182	1.53
⋮	
5400	$3.53 = \kappa_\infty$

Solvent. Methanol, 25° C.

	$10^4\kappa$, Ohm^{-1} Cm.$^{-1}$
0	0
27	0.352
35	0.487
48	0.646
55	0.732
62	0.813
70	0.900
79	0.969
86	1.07
93	1.12
100	1.21
105	1.26
114	1.33
120	1.40
⋮	
10800	$3.50 = \kappa_\infty$

Three liters of commercial dioxane were refluxed for 7 hours with 300 cc. of 1*N* HCl. Excess NaOH (pellets) was added, the mixture refluxed for 7 hours, and the water layer removed. The remaining liquid was dried over $CaCl_2$ for 6 days and then refluxed for 24 hours with sodium metal. The product was distilled through a 140-cm. column packed with steel helices. The fraction recovered at 102.0–4.0° C./740 mm. had $n_D^{22} = 1.4213$.

All reagents were stored in glass-stoppered bottles sealed with paraffin.

Solvent Mixtures. The solvent mixtures consisted of 13 to 17, 9 to 21, 5 to 25, and 0 to 30 ml. of dioxane to ml. of methanol, respectively. A micropipet calibrated to contain 0.005 ml. was used to introduce benzoyl chloride into the solvent mixture. This corresponds to an initial benzoyl chloride concentration of about $1.5 \times 10^{-3}M$.

Kinetic Measurements. Rates were measured by following the variation of the conductivity of the solution in a borosilicate glass conductivity cell with an Industrial Instruments, Inc., conductivity bridge (Type RC, Model 16B1). The procedure was similar to that previously described (*2*).

Table II. Pseudo-First-Order Rate Constants for Methanolysis of Benzoyl Chloride in Methanol–*p*-Dioxane Mixtures

Solvent Compn., Wt. % MeOH	ε (*3*), 25° C.	$k_1 \times 10^3$ (Sec.$^{-1}$) Temp., ° C. 24.0	30.0	34.9
52	15.7	1.91 ± 0.04	2.90 ± 0.05	4.05 ± 0.04
66	21.5	2.32 ± 0.04	3.52 ± 0.04	5.21 ± 0.04
81	26.8	3.00 ± 0.06	4.73 ± 0.03	6.81 ± 0.17
100	33.1	4.28 ± 0.07 (25.1° C.)	6.15 ± 0.22	8.57 ± 0.13

Table III. Activation Parameters for Methanolysis of Benzoyl Chloride in Methanol–*p*-Dioxane Mixtures

Compn. of Solvent, Wt. % MeOH	*E*, Kcal. Mole^{-1}	log *A*	$\Delta S^{\ddagger}$, Cal. Deg.$^{-1}$ Mole^{-1} at 30° C.
52	12.55 ± 0.67	6.51	−30.8
66	13.51 ± 0.54	7.29	−27.2
81	13.73 ± 0.87	7.57	−25.9
100	12.97 ± 0.68	7.14	−27.9

Calculations. Rate constants were calculated from the integrated first-order rate equation in the form

$$k_1 t = \ln \frac{\kappa_\infty - \kappa_0}{\kappa_\infty - \kappa_t}$$

where κ_0, κ_t, and κ_∞ are the conductivities at time 0, t, and ∞, respectively. In each case, k_1 was calculated with data extending to one-half life of the reaction. Justification for this procedure was derived from differential plots made for each composition at one temperature, which yielded good straight lines for $\frac{d\kappa_t}{dt}$ *vs.* t covering the reaction to better than 90% completion.

The values of the activation energy, E, and the frequency factor, A, were calculated by a least squares fit of the rate constant to the Arrhenius equation, $k_1 = Ae^{-E/RT}$. The error limits quoted for E are the maximum errors as determined by the method of Purlee *et al.* (*6*). The values of the entropy of activation were calculated from the equation $\Delta S^\ddagger = R\ln\left(\frac{Ah}{ekT}\right)$.

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Weathering and Stability of Methylacetylene-Propadiene-Hydrocarbon Mixtures

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When vapor is removed from a vessel containing a liquid hydrocarbon mixture, a simple batch distillation without rectification (called weathering) occurs. The compositions of liquid in equilibrium with vapor for the weathering of a stabilized methylacetylene-propadiene mixture were determined. These measured data agreed well with the composition predicted by the theory of regular solutions. The stability of the vapor compositions was determined by a 100-joule fuse-wire ignition test; the vapor samples were stable throughout depletion due to weathering.

THE POTENTIAL HAZARDS of mixtures containing methylacetylene and propadiene (allene), as well as methods for stabilizing such mixtures, have been reported (*4*, *5*). A stabilized mixture of methylacetylene and propadiene (commercially available as MAPP Gas, The Dow Chemical Co., Midland, Mich.) is used for applications such as metal cutting, welding, brazing, flame hardening, heating, and metallizing.

In the course of using the stabilized methylacetylene-propadiene vapor from a cylinder, the composition of the material remaining in the cylinder changes. Essentially, a differential distillation occurs; this is called "weathering."

The present investigation was carried out to measure the change in vapor and liquid composition due to weathering and also to check the stability of the vapor as a cylinder of liquid was depleted.

EXPERIMENTAL APPARATUS AND PROCEDURE

Weathering. Commercial cylinders (about 40 pounds net weight) of a stabilized methylacetylene-propadiene mixture were depleted at 0.5 to 3.0 pounds per hour (typical continuous withdrawal rates for industrial applications) by withdrawing vapor from the top of the cylinders. This weathering was done at ambient temperature; calculations showed that the vapor-liquid equilibrium compositions were very little affected by small changes in temperature.

Stability Measurements. At various levels of depletion of the stabilized methylacetylene-propadiene mixture—0, 20, 30% (weight), etc., depletion—samples of vapor were passed into a 10 1/2-inch i.d. spherical bomb equipped with a 2200-p.s.i.g. frangible safety disk. Previous work using this type of apparatus and testing similar compositions is described by Yoshimine *et al.* (*5*). The vapor in the bomb was taken to a temperature of 68° C. and a pressure of 220 p.s.i.g. Then at least three attempts to ignite the vapor were made by discharging 100 joules of electrical energy across a 1-inch length of 30-gage platinum wire. This amount of energy caused the fuse wire to vaporize with a sharp crack like a fire cracker. If no decomposition of the sample was observed, the sample was considered stable.