tonitrile extract. One advantage of the HPLC method is that it allows the simultaneous determination of TCB and PCB. The quantity of adsorbent required for a transformer fluid cleanup is dependent upon the total concentration of chlorine-containing contaminants (TCB and PCB). The HPLC method is capable of measuring PCB levels well below the limits specified by state and federal regulations for the transformer fluid application.

The gas chromatographic procedure for PCB levels >5 ppm is quite simple and straightforward. A solvent dilution of the sample is the only preparation required. Samples with PCB levels >500 ppm require successive dilutions to keep sample and standard concentrations comparable. For samples containing 25 ppb to 5 ppm PCB, the charcoal column extraction procedure separates the PCB from the siloxane fluid and produces a siloxane-free concentrate which can be analyzed by electron capture. As with HPLC, the lower detection limit is dependent upon the presence of extraneous contaminants which can interfere with the measurements.

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Substituent and Solvent Effects in the Kinetics of N-Alkylimidazole-Catalyzed Reaction of Acetic Anhydride with Isopropyl Alcohol

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The overall rate of the N-methylimidazole-catalyzed reaction of acetic anhydride with isopropyl alcohol is rather insensitive to the solvent polarity. Of the nine solvents studied, N,N-dimethylformamide is the best for practical analytical use. A series of N-alkyl substituted imidazoles was investigated as catalysts in this reaction. The most effective catalyst was N-n-pentylimidazole, which is about 60% more reactive than N-methylimidazole.

N-Methylimidazole (NMIM) was recently introduced as a catalyst for analytical acetylations of hydroxy compounds (1, 2). Among the advantages of NMIM for this purpose are its moderate basicity, liquid state at room temperature, solvent power, and high catalytic efficiency, which is about 4×10^2 greater than that of pyridine in the reaction of acetic anhydride with isopropyl alcohol. As a reasonable extension of this work, the effect of modification of the N-substituent on catalytic power has been investigated. For practical analytical purposes and mechanistic reasons, the effect of the reaction solvent on the rate has also been studied.

EXPERIMENTAL

Materials. Solvents and reagents were the best commercially available grades and were used directly.

The synthesis of N-ethylimidazole is typical of the preparation of N-alkylimidazoles (3). Sixty-eight grams of imidazole (2-methylimidazole was the starting material in the synthesis of 2-methyl-N-ethylimidazole) was dissolved in 100 mL of methanol, 120 mL of 10 M NaOH was added, followed by the dropwise addition, with stirring, of 107 mL of iodoethane. The temperature, which was 20 °C initially, was maintained between 30 and 40 °C during this process, which took about 3.5 h. The solution was allowed to stand for 2 h, the solvent was removed under reduced pressure, and the residue was mixed with 150 mL of chloroform.

The chloroform solution was dried with sodium sulfate, the chloroform was removed by distillation, and the residue was purified by distillation under reduced pressure. The product was characterized by elemental analysis (Galbraith Laboratories, Knoxville, Tenn.) and proton magnetic resonance (4). Compounds prepared in this way were N-ethylimidazole, N-n-butylimidazole, N-n-pentylimidazole, N-n-hexylimidazole, and N-ethyl-2-methylimidazole.

Procedures. *Kinetic Measurements.* The N-alkylimidazole, the solvent, and solutions of the anhydride and of isopropyl alcohol were separately brought to temperature in a constant-temperature water bath. Appropriate volumes were mixed in a 125-mL glass-stoppered flask to initiate the reaction. A blank solution, identical with the sample except that it contained no alcohol, was also prepared. At recorded times, 5.0-mL portions of the reaction mixture were withdrawn, discharged into 20 mL of water, and allowed to cool to room temperature. The solutions were then titrated to the thymolphthalein end point with standard 0.5 M NaOH. With the volumes of titrant consumed by the blank and the sample, and the initial concentrations of anhydride and alcohol, the conventional second-order plot was made. These plots were linear over 95% of the time course of the reaction.

pKₐ′ Measurements. pK_a' was measured potentiometrically at 25 °C. For the N-pentyl and N-hexyl compounds, the water solubilities were too low to permit pK_a' measurement in water, so the apparent pK_a' was obtained in several aqueous ethanol mixtures, and extrapolation to 0% ethanol yielded the pK_a' in water. The ionic strength was 0.02 M. The reproducibility of pK_a' was 0.02–0.12.

RESULTS AND DISCUSSION

Third-Order Rate Constants. The simplest kinetic interpretation of this system is according to rate equation 1,

$$V = k_3[\text{Ac}_2\text{O}][\text{ROH}][\text{N}] \qquad (1)$$

where Ac_2O, ROH, and N represent acetic anhydride, isopropyl alcohol, and the catalyst (N-alkylimidazole), respectively, and brackets signify molar concentrations. Since the

Table I. Third-Order Rate Constants for NMIM-Catalyzed Acetylation of Isopropyl Alcohol at 45 °C

solvent	$10^3 k_3/$ $M^{-2} s^{-1}$	μ	ϵ	E_T
ethyleneglycol dimethyl ether	2.56	1.71	7.20	38.2
dimethylsulfoxide (DMSO)	3.58	4.49	46.6	45.0
dioxane	3.66	0.45	2.21	36.0
ethyl acetate	4.00	1.81	6.02	38.1
acetonitrile	4.36	3.84	37.5	46.0
methyl ethyl ketone (MEK)	4.40	2.82	18.5	41.3
pyridine	5.70^a	2.19	12.3	40.2
N,N-dimethylformamide (DMF)	7.35	3.82	36.7	43.8
tetramethylene sulfone (sulfolane)	12.8	4.9	44.0	44.0

^{a} Corrected for concurrent catalysis by pyridine.

total catalyst concentration, N_t, was constant throughout a reaction, k_3 was calculated with Equation 2, where k_{obsd} is the observed apparent second-order rate constant.

$$k_3 = k_{obsd}/N_t \qquad (2)$$

Some experiments were made in order to detect possible concentration dependencies of k_3. In N,N-dimethylformamide (DMF) as solvent, at 45 °C, with initial concentrations $[Ac_2O]_0$ = 0.88 M, $[ROH]_0$ = 0.46 M, N_t = 1.4 M, the mean value of k_3 was 7.35 × 10^{-3} M^{-2} s^{-1}, with standard deviation 0.36 × 10^{-3} M^{-2} s^{-1} (n = 3); the catalyst was N-methylimidazole. Repetition at $[Ac_2O]_0$ = 0.94 M, $[ROH]_0$ = 0.37 M, and N_t = 0.3 M gave k_3 = 6.4 × 10^{-3} M^{-2} s^{-1}, standard deviation 0.5 × 10^{-3} M^{-2} s^{-1}, and n = 5 (different worker). At constant $[Ac_2O]_0$ and $[ROH]_0$, k_{obsd} was a linear function of N_t, from N_t = 0.2 to 1.4 M. The limits of initial concentrations studied were 0.95–4.77 M for $[Ac_2O]_0$; 0.18–1.90 M for $[ROH]_0$; 0.2–4.7 M for N_t; the k_3 values ranged from 6.2 × 10^{-3} M^{-2} s^{-1} to 8.0 × 10^{-3} M^{-2} s^{-1}, with no evident trend with concentration. It is therefore concluded that over these concentration ranges, which are typical of those that might be encountered in a titrimetric analysis of a hydroxy sample, k_3 does not vary significantly.

The temperature dependence of the $Ac_2O/ROH/NMIM$ system in DMF was determined from k_3 measurements at four temperatures in the range 25–45 °C. From the linear Arrhenius plot, the quantities $\Delta H^\ddagger$ = 4.8 kcal/mol and $\Delta S^\ddagger$ = −54 eu were evaluated.

The third-order rate constant for the NMIM-catalyzed acylation of isopropyl alcohol in DMF at 45 °C was measured for reactions with three anhydrides. The results were (standard deviation in parentheses, n = 3–5): acetic anhydride, k_3 = 6.4 × 10^{-3} M^{-2} s^{-1} (0.5 × 10^{-3}); phthalic anhydride, k_3 = 1.1 × 10^{-3} M^{-2} s^{-1} (0.02 × 10^{-3}); succinic anhydride, k_3 = 4.2 × 10^{-5} M^{-2} s^{-1} (0.3 × 10^{-5}).

Solvent Effects. Table I gives k_3 values for the reaction of Ac_2O with isopropyl alcohol catalyzed by NMIM in nine solvents. The table also gives some measures of solvent polarity, namely, dipole moment μ, dielectric constant ϵ, and the molar transition energy, E_T, of a solute (5). The reaction in tetrahydrofuran gave anomalous kinetic behavior, which was therefore not included in Table I. The precision of these measurements is comparable with that reported above in DMF. The rate constant appears to be remarkably insensitive to the nature of the solvent, the maximum relative rate in Table I being 5:1. Since sulfolane is a solid at room temperature, DMF is the most practical of these solvents for routine analytical use.

As Table I shows, k_3 is rather insensitive to changes in solvent polarity, or rather the data show no clear trend with measures of solvent polarity. The solvents studied are all hydrogen-bond acceptors or electron-pair donors. Several of them are dipolar aprotic solvents. In part, because of the very limited range of k_3 values, these data do not correlate well with any available measures of solvent polarity (the three listed in Table I being typical). For example, dimethyl sulfoxide and sulfolane appear to be of comparable polarity, yet the difference in k_3 in these solvents is clearly significant. The most likely conclusion is that k_3 is nearly independent of solvent polarity but that moderate medium effects may be produced by specific interactions such as solvation.

Substituent Effects in the Catalyst. Table II gives the N-substituted imidazoles studied here, their pK_a' values, and their k_3 values for the acetic anhydride/isopropyl alcohol reaction at 45 °C in DMF. (The different values for NMIM in Tables I and II are by different observers and are used to maintain consistency within a set of comparative measurements.)

The first five entries in Table II show that k_3 is slightly but significantly dependent upon the N-substituent in a series of N-n-alkyl substituted imidazoles; k_3 is maximal for the n-pentyl compound. Although the catalyst basicity is practically invariant within the series, the rate effect is in the direction expected on the basis of Taft's polar substituent constants. The low value of k_3 for the N-benzylimidazole may be ascribed to electron withdrawal by the substituent. A steric effect is probably responsible for the low catalytic effectiveness of N-ethyl-2-methylimidazole. 2-Picoline and 2,6-lutidine gave no detectable catalysis under the same conditions, indicating somewhat different geometry in the imidazole and pyridine series.

Because of the modest effect of the substituent on the rate, the readily available N-methylimidazole is the preferred catalyst for acetylations in analyses of the kinds described earlier (1, 2). There may be circumstances, however, in which the other compounds become preferred catalysts. (They are, after all, more effective than NMIM.) For example, separation of the catalyst from reaction products may be an important factor in some analytical or synthetic applications, and then the catalysts with longer N-alkyl substituents, which have lower water solubilities, may become the catalysts of choice.

Table II. Third-Order Rate Constants for Reaction of Acetic Anhydride with Isopropyl Alcohol Catalyzed by N-Substituted Imidazoles^a

R		R'	$10^3 k_3/M^{-2}$ s^{-1} ^{b}	$pK_a',$ 25 °C
H		CH_3	6.4 (0.5)	7.05
H		CH_2CH_3	8.6 (0.4)	-
H		$(CH_2)_3CH_3$	9.2 (0.02)	7.10
H		$(CH_2)_4CH_3$	10.3 (0.3)	7.12
H		$(CH_2)_5CH_3$	8.1 (0.5)	7.20
CH_3		CH_2CH_3	1.0 (0.08)	8.09
H		$CH_2C_6H_5$	2.8 (0.1)	6.65

^{a} At 45 °C in DMF. ^{b} Standard deviation in parentheses (n = 3).

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