

FAILURE OF FUNDAMENTAL RATE CONSTANT EXPRESSIONS FOR THE GASEOUS IONIC  
ACETYLTATION OF 2-ALKYLPYRIDINES

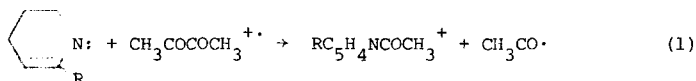
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We have established that no current physical model of ion-molecule reactivity explains the relative rates of a series of gaseous ion-molecule reactions (eq. 1). For the series R = H,



CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, *i*-C<sub>3</sub>H<sub>7</sub>, *t*-C<sub>4</sub>H<sub>9</sub>, the relative rates  $k_{\text{RPy}}/k_{\text{Py}}$  (determined by competitive acetylation of equimolar binary mixtures of nearest homologs at a low fraction of conversion of the precursor CH<sub>3</sub>COCOCH<sub>3</sub><sup>+·</sup> in an ion cyclotron resonance spectrometer<sup>1</sup>) are 1.0, 1.1, 0.23, 0.14, 0.08. The only precursor to RC<sub>5</sub>H<sub>4</sub>NCOCH<sub>3</sub><sup>+</sup> is CH<sub>3</sub>COCOCH<sub>3</sub><sup>+·</sup>, except for a very small contribution from (CH<sub>3</sub>CO)<sub>3</sub><sup>+</sup> and CH<sub>3</sub>CO<sup>+</sup> or from C<sub>5</sub>H<sub>4</sub>RN<sup>+·</sup> when R is H or CH<sub>3</sub>. In these cases the interference is not sufficient to alter the rates beyond our error limit (~20% for triplicate experiments on different days) and certainly not to alter the reactivity order. Study of some mixtures of homologs separated by 28 mass units confirmed these numerical results to within 10%.

The original expression for the rate of a bimolecular ion-molecule reaction involving intimate orbiting encounters was reported by Gioumousis and Stevenson.<sup>2</sup> In eq. 2,  $\alpha$  is the mean

$$k = 2\pi e (\alpha/\mu)^{1/2} \quad (2)$$

electric polarizability and  $\mu$  the reduced mass. Inclusion of a dipole moment term, suggested by

Moran and Hamill,<sup>3</sup> (eq. 3), gives rate constants calculated to be higher than found experimen-

$$k = \frac{2\pi e}{\mu^{1/2}} [\alpha^{1/2} + \mu_D (2/\pi kT)^{1/2}] \quad (3)$$

tally.<sup>4</sup> Su and Bowers therefore have recently suggested<sup>5</sup> a correction term  $c$ , set by them at 0.15 to fit experimental data for substituted ethylenes and benzenes (eq. 4). In eqns. 2 and 3,  $\mu_D$

$$k = \frac{2\pi e}{\mu^{1/2}} [\alpha^{1/2} + c\mu_D (2/\pi kT)^{1/2}] \quad (4)$$

is the dipole moment of the neutral.

In Table 1 are gathered the polarizabilities of the pyridines, their dipole moments, and the rate constants relative to pyridine. The polarizability of pyridine was derived from INDO molecular orbital calculations<sup>6</sup> and confirmed from experimental data used to obtain the dipole moment in benzene.<sup>7</sup> The polarizabilities of the alkyipyridines were derived from results of Beran and Kevan's favored method.<sup>8</sup> The dipole moments were obtained from an INDO/2 program and for those members of the series for which experimental data had been reported, were found to agree within 5% of the reported values. The trend of the dipole moments found experimentally was reproduced by the calculated values.

Table 1. Calculated Relative Rate Constants and Related Data for the Reaction of 2-Alkyl-pyridines and Biacetyl Molecular Ion

	Py	2-CH <sub>3</sub>	2-C <sub>2</sub> H <sub>5</sub>	2-i-C <sub>3</sub> H <sub>7</sub>	2-t-C <sub>4</sub> H <sub>9</sub>
$\alpha$ (in Å <sup>3</sup> )	8.8	10.8	12.8	14.8	16.8
$\mu_D$ (in D; INDO)	2.16	2.08	1.96 <sup>a</sup>	2.08	2.05
$k/k_{PY}$ (eq. 2)	1.0	1.06	1.12	1.18	1.22
$k/k_{PY}$ (eq. 3)	1.0	0.95	0.94	0.95	0.95
$k/k_{PY}$ (eq. 4) <sup>b</sup>	1.0	1.02	1.04	1.09	1.09

(a) experimental value in neat liquid<sup>9</sup>

(b)  $c = 0.15$

Quite clearly, the observed values indicate that some factor has until now been omitted from calculations. Thus, the observed results differ from the best calculated results (presum-

ably from eq. 4) by factors of 1.1 for methyl, 0.22 for ethyl, 0.13 for isopropyl, and 0.07 for t-butyl. These factors show no uniform trend and therefore must be composites of several parameters. The observation of increased nucleophilicity ( $k/k_{\text{Py}} = 1.1$ ) for 2-methylpyridine, noted above, is in concord with the substituent polarizability concepts of Schubert<sup>10</sup> and Brauman.<sup>11</sup> It is also in agreement with the so-called inductive effects expected for alkyl groups in solution<sup>12</sup> and with Brown's results for pyridines in solution,<sup>13</sup> though we point out that the concept of inductive effects of alkyl groups has little utility in the gas phase.<sup>11</sup> Obviously there is now a second, and new, parameter needed for the gaseous phase, which we suggest is related to the size of the alkyl group and may represent steric interference with the approach of the acetyl-transferring species to the reactive site of the neutral. While this concept is well established in solution chemistry,<sup>13</sup> only qualitative examples have been reported for the gas phase.<sup>14</sup> This work thus represents the first definitive test of current theories against this hypothesis, and they fail badly.

Acetylation in the gas phase has been found to respond like a typical solution electrophilic substitution to substituent effects in aromatic systems.<sup>1</sup> Since in solution the pyridine ring is deactivated to electrophilic substitution, we might assume that gaseous ionic acetylation occurs at the nitrogen atom, and that the reactivity shown is a manifestation of typical ortho-alkyl steric effects. However, there are many surprises<sup>1,11</sup> in experimental reactivity rankings in gaseous ion-molecule reactions, and we wish to defer this explanation until further studies of reactivity of other substituted pyridines can be made. For the moment, we note that incomplete work on gaseous ionic acetylation of 2,6-dialkylpyridines suggests a confirmation of these ideas. The rate of reaction of 2,6-d-t-butylpyridine is so low that it cannot be measured under the conditions<sup>15</sup> that we have used in this study.

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- (15) An ICR-9 spectrometer was used, with the standard flat cell; pressures: 2  $\mu$ torr pyridine mixture, 20  $\mu$ torr biacetyl; ionizing voltage, 14.6 eV; emission: 0.1-0.2  $\mu$ a for single, 50 na for double resonance experiments. Five  $\mu$ l pyridine mixture was injected into a 200-ml bulb and thence admitted to the cell through a standard leak valve. Results at various inlet temperatures and times and calibration experiments indicated that the mixtures did not fractionate. No decomposition of  $\text{RC}_5\text{H}_4\text{NCOCH}_3^+$  was observed.