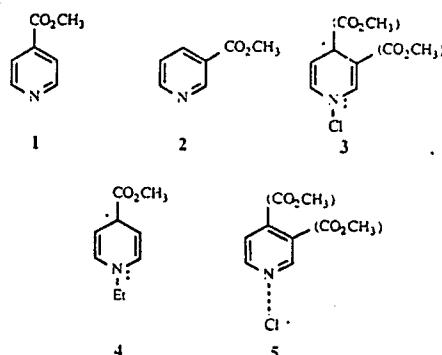


full or loose bond? What are the kinetic and selectivity properties of these complexes?

We have addressed these questions by three techniques: classic chlorination selectivity studies,⁴⁻⁶ nanosecond laser spectroscopy and kinetics,⁶ and molecular orbital calculations. All three approaches point to similar conclusions.

Photochemically initiated free radical chain chlorination (Cl_2) of 2,3-dimethylbutane (DMB) is reported⁵ to show a selectivity ($k_{\text{tertiary}}/k_{\text{primary}}$) of ca. 50/1 at 4 M benzene in CCl_4 and low DMB concentrations, a result we have confirmed in CCl_4 solution. With pyridine instead we find that the selectivity becomes 200/1 ($\pm 20\%$) at 4 M pyridine and DMB concentrations below 0.1 M. As Skell reported for benzene,⁵ our selectivity climbs to a plateau as the DMB concentration is lowered, but no plateau is found on increasing the pyridine concentration; selectivities at a low DMB concentration (vs pyridine concentration) are 95 (2 M), 46 (1 M), 28 (0.5 M), and 18 (0.25 M). This indicates that at a DMB concentration below 0.1 M the $\text{Cl}\cdot$ equilibrates with its pyridine complex before attacking DMB but that attack on DMB involves both the complex (high selectivity) and the free $\text{Cl}\cdot$ in equilibrium (low selectivity).

With methyl isonicotinate (1) at 4 M the selectivity is decreased to 140/1, while with methyl nicotinate (2) at 4 M the selectivity is slightly less at 120/1. In these cases as well the plateau occurred



on lowering the DMB concentration but not on raising the pyridine derivative concentration. Thus all three compounds produce more selectivity than does benzene and presumably bind $\text{Cl}\cdot$ more strongly. However, the finding that the pyridine esters show less selectivity than does pyridine itself is not consistent with a fully formed σ -bond in the complexes. The ester groups should strongly stabilize the resulting π^* -type radicals 3 by conjugation³ and increase the binding constant for $\text{Cl}\cdot$. If instead the complex involves weak electron donation by the pyridine to the chlorine atom, the decreased basicity of the pyridine esters could explain our findings.

Solutions of Cl_2 in CCl_4 with aromatic complexes were irradiated with a Quanta Ray (6 ns FWHM, 3.5 mJ, 355 nm) Nd-YAG laser. Spectra were obtained with a Parc OMA III optical multichannel analyzer calibrated with a mercury lamp. With use of benzene we observed the reported chlorine atom complex^{6,7} with λ_{max} 490 nm, while with pyridine the complex had λ_{max} 334 nm. A Stern-Volmer plot of the intensity of the complex at 370 nm as a function of DMB concentration gave a rate constant⁸ for formation of the pyridine complex of $1.5 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ (reported⁶ for benzene $0.6 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$). The formed complexes also decayed by second-order reactions with DMB. Benzene (0.25 M) showed a second-order rate constant⁸ of $4.4 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$, while pyridine (0.25 M) showed $2.6 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$. At these aromatic concentrations the decay involves chiefly reversible dissociation of the complex to free $\text{Cl}\cdot$, which is scavenged by DMB. Thus the pyridine/ $\text{Cl}\cdot$ association constant is ca. $34\,000 \text{ M}^{-1}$, 170 times

(8) With a significant radical chain, $\text{Cl}\cdot$ can be recycled. This would cause an overestimate of the rate of complex formation and an underestimate of its rate of reaction. Without degassing the solutions, our data for benzene are similar to the best values in ref 6; thus we assume that with the pyridine compounds trapping by dissolved O_2 also suppresses most of the recycling problem.

Pyridine Complexes of Chlorine Atoms

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The use of pyridine ester templates to direct selective steroid chlorinations has been described.³ The results indicate that a chlorine atom coordinates to the pyridine nitrogen and is then relayed to a geometrically accessible substrate hydrogen. Although many studies have been reported on chlorine atom complexes to benzene and its derivatives,⁴⁻⁷ pyridine raises some unique questions. Is the chlorine σ bonded to N or π bonded? Is it a

(1) Columbia University.

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(3) Breslow, R.; Brandl, M.; Hunger, J.; Adams, A. D. *J. Am. Chem. Soc.* 1987, 109, 3799-3801.

(4) Russell, G. A. *J. Am. Chem. Soc.* 1957, 79, 2977-2978. Russell, G. A. *J. Am. Chem. Soc.* 1958, 80, 4987-4996. Walling, C.; Mayahi, M. F. *J. Am. Chem. Soc.* 1958, 81, 1485-1489.

(5) Skell, P. S.; Baxter, H. N., III; Taylor, C. K. *J. Am. Chem. Soc.* 1983, 105, 120-121. Skell, P. S.; Baxter, H. N., III; Tanko, J. M.; Chebolu, V. J. *Am. Chem. Soc.* 1986, 108, 6300-6311.

(6) Bunce, N. J.; Ingold, K. U.; Landers, J. P.; Luszyk, J.; Scaiano, J. C. *J. Am. Chem. Soc.* 1985, 107, 5464-5472. Bunce, N. J.; Joy, R. B.; Landers, J. P.; Nakai, J. S. *J. Org. Chem.* 1987, 52, 1155-1156.

(7) Bühler, R. E.; Ebert, M. *Nature (London)* 1967, 214, 1220-1221. Bühler, R. E. *Helv. Chim. Acta* 1968, 51, 1558-1571.