terpretation of the metal effect on aldol-type stereoselection. Until now, it seems that the possibility through the α-metallo ketone form has been neglected. There is the possibility that erythro selection of triphenyltin enolates proceeds through the α-stannyl ketone form. Certain copper enolates, prepared from the conjugate addition of Me_2CuLi to α,β-unsaturated carbonyl compounds, undergo erythro-selective condensations.[22] This result can be explained by the intervention of α-cuprio ketones, and such species are frequently suggested in many other reactions.[23] The most recent reports on erythro-selective condensations are also interesting in this respect.[24]

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(21) If the transmetalation from Hg to B and subsequent formation of the boron enolate are involved, **1** and **2** should give the threo aldol due to their trans geometries.

(22) Heng, K. K.; Smith, A. J. *Tetrahedron* **1979**, *35*, 425. Heng, K. K.; Simpson, J.; Smith, R. A. *J. Org. Chem.* **1981**, *46*, 2932. See also: House, H. O.; Wilkins, J. M. *J. Org. Chem.* **1978**, *43*, 2443. Posner, G. H.; Lenz, C. M. *J. Am. Chem. Soc.* **1979**, *101*, 934.

(23) Berlan, J.; Battioni, J. P.; Koosha, K. *J. Organomet. Chem.* **1978**, 152, 359 and references cited therein.

(24) Reetz, M. T.; Peter, R. *Tetrahedron Lett.* **1981**, 4691. Shieh, H. M.; Prestwich, G. D. *J. Org. Chem.* **1981**, *46*, 4319.

(25) **Note Added in Proof**: After the submission of this paper, two conflicting papers on tin enolates appeared: threo selective reactions of isolated R_3Sn enolates (Shenvi, S; Stille, J. K. *Tetrahedron Lett.* **1982**, 627) and erythro selective condensations of divalent tin enolates (Mukaiyama, T.; Stevens, R. W.; Iwasawa, N. *Chem. Lett.* **1982**, 353).

Nitrogen to Nitrogen Proton Transfer. Significance of Large Negative Entropies of Activation

Charles L. Perrin* and Wei-hsien Wang

Department of Chemistry, University of California
San Diego, La Jolla, California 92093

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In studying the kinetics of proton exchange of *N*,*N*-dimethylcyclohexylamine hydrochloride, catalyzed by bases such as pyridine (eq 1, R = cHx), Menger, Singh, and Bayer[1] have

$$RNHMe_2^+ + Py \xrightarrow{k_2} RNMe_2 + PyH^+ \qquad (1)$$

observed that $\Delta S^\ddagger$ in chloroform as solvent is large and negative, ca. −30 eu. They also found a Hammett ρ value of −6.4 and a Brønsted β value of 1.1 (for variations of the catalyzing base) and normal reactivity for 2,6-di-*tert*-butylpyridine, without any steric retardation. These latter results suggested that the transition state resembles products, so that the charge contents of reactant and transition state would not differ appreciably. The large negative $\Delta S^\ddagger$ was then interpreted in terms of ion-pair dissociation. We now wish to show that eq 1 is not the correct mechanism for the proton exchange. Instead, we propose that the mechanism is a chain reaction, with eq 1 as initiation step and with a propagation step whose transition state is consistent with a large negative $\Delta S^\ddagger$.

The mechanism of any exchange reaction must be symmetrical.[2] To take eq 1 as the rate-limiting step implies that its reverse must also be the rate-limiting step, since the transition states are identical. We therefore should adapt eq 1 by explicitly writing it as reversible (eq 2). Of course, the PyH^+ must return a

$$RNHMe_2^+ + Py \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} RNMe_2 + PyH^+ \qquad (2)$$

different proton to the amine, in order to qualify as exchange. However, we are then led to consider whether PyH^+ is the only acid that can return a proton.

Might $RNHMe_2^+$ also serve (eq 3)? Each occurrence of either

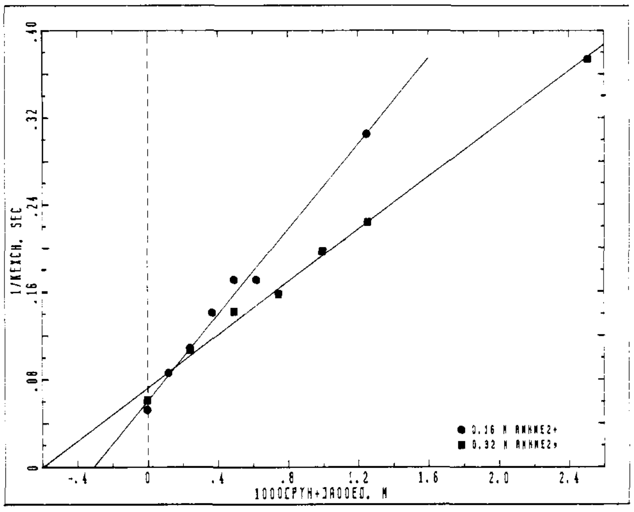

Figure 1. Kinetics of proton exchange of *N*,*N*-dimethylcyclohexylamine hydrochloride (0.16 and 0.32 M) in chloroform at 34 °C, catalyzed by 2.47×10^{-3} M added Py and inhibited by added PyH^+.

$$RNHMe_2^+ + RNMe_2 \overset{k}{\rightleftharpoons} RNMe_2 + RNHMe_2^+ \qquad (3)$$

eq 2 or eq 3 represents one proton exchange, but which is faster? Even though $RNHMe_2^+$ is a much weaker acid than PyH^+, rate constants for thermoneutral proton transfer involving nitrogen or oxygen are nearly as large as those for exergonic proton transfers.[3] Therefore the *rate* of protonation by the more abundant $RNHMe_2^+$ is likely to be even greater than the rate of protonation by PyH^+. Thus we expect eq 3 to be a faster reaction than eq 2. This suggests that the dominant mechanism of exchange is likely to be eq 3, utilizing $RNMe_2$ generated through eq 2. Moreover, the mechanism of eq 3 automatically satisfies the requirement for symmetry. However, this leads to eq 4, which

$$v = k_{exch}[RNHMe_2^+] = k[RNHMe_2^+][RNMe_2] \qquad (4)$$

does not fit Menger's observed kinetics, which is first order in $RNHMe_2^+$ and first order in Py (eq 5). Even if eq 4 is trans-

$$v = k_{exch}[RNHMe_2^+] = k_2[RNHMe_2^+][Py] \qquad (5)$$

formed by assuming that the steady-state $[RNMe_2]$ is governed by the equilibrium of eq 2, with equilibrium constant $K_e = k_2/k_{-2}$, the result (eq 6) still does not fit the observed kinetics, which is *not* second order in $RNHMe_2^+$.

$$v = k_{exch}[RNHMe_2^+] = kK_e\,[RNHMe_2^+]^2[Py]/[PyH^+] \qquad (6)$$

It is the purpose of this paper to demonstrate that eq 6 nevertheless describes the kinetics of the exchange. Equation 6 may be reconciled with eq 5, observed by Menger, if $[RNHMe_2^+]/[PyH^+]$ was constant throughout all Menger's kinetic runs. This would hold if the *N*,*N*-dimethylcyclohexylamine hydrochloride had been contaminated by some excess HCl, which would be converted to PyH^+ under the conditions of the kinetic experiments. Indeed, the presence of excess HCl may be inferred from the stated requirement that the amine hydrochloride must be free of traces of unprotonated amine. Such contamination has been demonstrated[4] previously even for amine salts recrystallized twice.

Figure 1 shows our evidence[5] in favor of eq 6 over eq 5. It is quite clear that adding PyH^+ decreases k_{exch}, whereas eq 1 and 5 imply that k_{exch} should be independent of $[PyH^+]$. The observed dependence on $[PyH^+]$ is sufficient to disprove eq 1 as the mechanism of exchange.

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(1) Menger, F. M.; Singh, T. D.; Bayer, F. L. *J. Am. Chem. Soc.* **1976**, *98*, 5011.

(2) Perrin, C. L.; Schiraldi, D. A.; Arrhenius, G. M. L. *J. Am. Chem. Soc.* **1982**, *104*, 196.

(3) Eigen, M. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 1.

(4) Cocivera, M. *J. Am. Chem. Soc.* **1966**, *88*, 672.

(5) Amine hydrochlorides were prepared from the amine (redistilled *N*,*N*-dimethylcyclohexylamine or Spectroquality pyridine) and HCl in ether. Kinetics of proton exchange in reagent chloroform were followed on a Varian EM-390 NMR spectrometer at 34 °C. Rate constants, including a statistical factor of 2, were determined from the valley-to-peak intensity ratio of the *N*-methyl doublet,[6a] as calculation from the line-shape equation.[6b]

(6) (a) Grunwald, E.; Jumper, C. F.; Meiboom, S. *J. Am. Chem. Soc.* **1962**, *84*, 4664. (b) Gutowsky, H. S.; Holm, C. H. *J. Chem. Phys.* **1956**, *25*, 1228.

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The total [PyH$^+$] is equal to the sum of the [PyH$^+$] added and the [PyH$^+$] produced from the excess HCl in the amine hydrochloride (eq 7). Therefore, according to eq 6 and 7, a plot of

$$[\mathrm{PyH^+}] = [\mathrm{PyH^+}]_{\mathrm{added}} + [\mathrm{HCl}]_0 \qquad (7)$$

$1/k_{\mathrm{exch}}$ vs. $[\mathrm{PyH^+}]_{\mathrm{added}}$ should be linear and intersect the horizontal axis at $-[\mathrm{HCl}]_0$. Figure 1 contains two such plots, and they are indeed linear ($r > 0.994$). From those intersections, we determine that our $[\mathrm{HCl}]_0$ was 0.59×10^{-3} and 0.31×10^{-3} M for [RNHMe$_2^+$] of 0.32 and 0.16 M, respectively. Thus, the ratio $[\mathrm{HCl}]_0/[\mathrm{RNHMe_2^+}]$ is constant, corresponding to a contamination by 0.19 mole % HCl. This value varied from batch to batch, so it is understandable that our k_{exch} at zero $[\mathrm{PyH^+}]_{\mathrm{added}}$ differs from that of Menger et al. With another batch of RNHMe$_2^+$Cl$^-$, we find contamination by 0.22 mole % HCl, and *this value, determined by kinetic analysis, could be verified independently* as 0.21 mole % by titration with NaOH in methanol. Neutralization of this HCl with RNMe$_2$ produces a solution that shows extremely fast (k_{obsd} ca. 10^3 s^{-1}) pyridine-catalyzed proton exchange, as expected from our mechanism. The fact that Menger et al. observed conveniently measurable rates is evidence that their amine hydrochloride too contained excess HCl.

It also follows from eq 6 and 7 that the slope of $1/k_{\mathrm{exch}}$ vs. $[\mathrm{PyH^+}]_{\mathrm{added}}$ is $1/kK_e[\mathrm{RNHMe_2^+}][\mathrm{Py}]$. We may correct the [Py] for the amount that is converted to PyH$^+$ by the HCl contamination. Then from the slopes in Figure 1 we may determine that $kK_e = 13.8$ and 14.9 M^{-1} s^{-1} for [RNHMe$_2^+$] of 0.32 and 0.16 M, respectively. The constancy of this rate constant, over a 2-fold variation in [RNHMe$_2^+$], is strong evidence for eq 6 and the mechanism of eq 3.

This mechanism represents a chain reaction, for which RNMe$_2$ is the chain carrier, eq 3 is the propagation step, and the forward and reverse reactions of eq 2 are initiation and termination steps, respectively. As stated above, protonation of RNMe$_2$ by RNHMe$_2^+$ (the propagation step) may be much more frequent than protonation by PyH$^+$ (termination). This is the condition of long chains, and steady-state analysis of eq 2 and 3 then leads to eq 6. Without the assumption of long chains, steady-state analysis leads to eq 8. The influence of the second term in eq

$$v = k_{\mathrm{exch}}[\mathrm{RNHMe_2^+}] = kK_e[\mathrm{RNHMe_2^+}]^2[\mathrm{Py}]/[\mathrm{PyH^+}] + k_2[\mathrm{RNHMe_2^+}][\mathrm{Py}] \qquad (8)$$

8 can be seen as a slight curvature in Figure 1, and kinetic data at higher concentrations of Py and PyH$^+$ (off scale in Figure 1) indicate that $k_2 = 1.4 \times 10^2$ M^{-1} s^{-1}. This value corresponds to a chain length of 50 under the conditions of Figure 1 with no added PyH$^+$. Also, from kK_e and k_2, we obtain $k/k_{-2} = 0.1$, which corroborates the statement above comparing rate constants for thermoneutral and exergonic proton transfers.

We are especially interested in the propagation step (eq 3). Unfortunately we cannot determine k for this step alone, but only kK_e. However, if K_e (eq 2) is the same in chloroform as it is in aqueous solution,[7] then $k = 5 \times 10^6$ M^{-1} s^{-1}. This value is consistent with the upper limit of 3×10^7 M^{-1} s^{-1} for triethylamine (eq 3, R = Me) in aqueous solution,[8] which is the only other rate constant reported for symmetrical proton transfer between tertiary amines.

This mechanism accounts for Menger's observed results. Comparison of eq 4, 6, and 7 shows that the k_2 of Menger et al.[1] is our $kK_e[\mathrm{RNHMe_2^+}]/[\mathrm{HCl}]_0$. Therefore their observed $\Delta H^{\ddagger}$ of 4 kcal/mol must equal $\Delta H^\circ + \Delta H^{\ddagger}$, where ΔH° and $\Delta H^{\ddagger}$ apply to eq 2 and 3, respectively. If ΔH° is the same in chloroform as it is in aqueous solution[7] (or even in the gas phase, for model amines[9]), then $\Delta H^{\ddagger} = 0$. It then follows that $\Delta S^{\ddagger}$ for eq 3 is ca. −28 eu, quite close to the value that Menger et al. originally reported. However, this value now applies to a symmetrical transition state rather than one resembling products. A similar value, −29 eu, was previously observed[4] for symmetrical proton transfer from trimethylamine hydrochloride to trimethylamine, but via a *tert*-butyl alcohol bridge. Such values are quite reasonable for such highly organized transition states, involving proton (and chloride) transfer from tertiary amine hydrochloride to tertiary amine. Also, the Hammett ρ of −6.4, the Brønsted β of 1.1, and the normal reactivity of 2,6-di-*tert*-butylpyridine all follow from the simple proportionality between k_{exch} and K_e (eq 6). These results are to be expected because a proton has already been transferred completely to the catalyzing base before the transition state (strictly, the propagation step) has been reached.

Acknowledgment. This research was supported by National Science Foundation Grant CHE78-12256.

Registry No. PyH$^+$, 16969-45-2; *N,N*-dimethylcyclohexylamine hydrochloride, 2498-24-0.

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[7] Christensen, J. J.; Izatt, R. M.; Wrathall, D. P.; Hansen, L. D. *J. Chem. Soc. A.* **1969**, 1212.

[8] Grunwald, E.; Ralph, E. K. In "Dynamic NMR Spectroscopy"; Jackman, L. M., Cotton, F. A., Eds.; Academic Press: New York, 1975; p 621.

[9] Aue, D. H.; Webb, H. M.; Bowers, M. T. *J. Am. Chem. Soc.* **1976**, *98*, 318.

Di-*tert*-butylcarbene: The Low-Temperature Photochemistry of Di-*tert*-butyldiazomethane

James E. Gano* and Richard H. Wettach

Department of Chemistry, Bowman-Oddy Laboratories
University of Toledo, Toledo, Ohio 43606

Matthew S. Platz and V. P. Senthilnathan

The Department of Chemistry, The Ohio State University
Columbus, Ohio 43210

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Interest continues in this and other laboratories[1] in the synthesis of twisted alkenes. This has prompted investigations into the potential coupling of "di-*tert*-butylcarbene fragments" to form the elusive[2] and highly sterically congested[3] tetra-*tert*-butylethylene. Our approach to this problem has utilized low-temperature methods in an effort to produce high concentrations of di-*tert*-butylcarbene so as to promote direct coupling. Although carbene coupling reactions are not common, there is precedent for this reaction at low temperatures.[4a] Coupling of two methylene triplets is expected to occur with little or not activation energy.[4b] Although tetra-*tert*-butylethylene was not detected, the carbene was found to be sufficiently stable to provide the *first direct observation of a hydrocarbon dialkylcarbene*.[4c,5]

Di-*tert*-butyldiazomethane was deposited on a cesium iodide window and cooled to 14 K by pyrolyzing its triphenylphosphine

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(1) (a) Gano, J. E.; Eizenberg, L. *J. Am. Chem. Soc.* **1973**, *95*, 972. (b) Back, T. G.; Barton, D. H. R.; Britten-Kelly, M. R.; Guziec, F. S., Jr. *J. Chem. Soc., Perkin Trans. 1* **1976**, 2079. (c) Barton, D. H. R.; Guziec, F. S., Jr.; Shahak, I. *J. Chem. Soc., Perkin Trans. 1*, **1974**, 1794. (d) Krebs, R.; Ruger, W. *Tetrahedron Lett.* **1979**, 1305. (e) Gerson, F.; Lopez, J.; Krebs, A.; Ruger, W. *Angew. Chem., Int. Ed. Engl.* **1981**, *95*, 20. (f) Sakuari, H.; Nakadaira, Y.; Kira, M.; Tobita, H. *Tetrahedron Lett.* **1980**, 3077. (g) Sakuari, H.; Tobita, H.; Kira, M.; Nakadaira, Y. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 610.

(2) (a) Barton, D. H. R.; Buziec, F. S. Jr.; Shahak, I. *J. Chem. Soc., Perkin Trans. 1*, **1974**, 1797. (b) Back, T. G.; Barton, D. H. R.; Britten-Kelly, M. R.; Guziec, F. S., Jr. *J. Chem. Soc., Chem. Commun.* **1975**, 539. (c) Back, T. G.; Barton, D. H. R.; Britten-Kelly, M. R.; Guziec, F. S., Jr. *J. Chem. Soc., Perkin Trans. 1* **1976**, 2079. (d) Olah, G. A. Parkash, G. H. Surya *J. Org. Chem.* **1977**, *42*, 580.

(3) (a) Ermer, O.; Lifson, S. *J. Am. Chem. Soc.* **1973**, *95*, 4121. (b) Ermer, O.; Lifson, S. *Tetrahedron* **1974**, *30*, 2425. (c) Lenoir, D.; Danner, H.; Frank, R. M. *Chem. Ber.* **1980**, *113*, 2636. (d) Burkert, V. *Tetrahedron* **1981**, *37*, 33.

(4) (a) Baird, M. S.; Dunkin, I. R.; Hacker, N.; Poliakoff, M.; Turner, J. J. *J. Am. Chem. Soc.* **1981**, *103*, 5190. (b) Cheung, L. M.; Sundberg, K. R.; Ruedenberg, K. *J. Am. Chem. Soc.* **1978**, *100*, 8024. (c) As suggested by a referee, it is possible that tetra-*tert*-butylethylene is formed by carbene coupling and is photochemically destroyed under the reaction conditions. We saw no evidence of other intermediates.

(5) (a) Moss, R. W.; Jones, M., Jr. "Reactive Intermediates"; Wiley-Interscience: New York, 1978; pp 69-116. (b) Gaspar, P. P.; Hammond, G. S. *Carbenes* **1975**, *2*, 207-362.

0002-7863/82/1504-2326$01.25/0