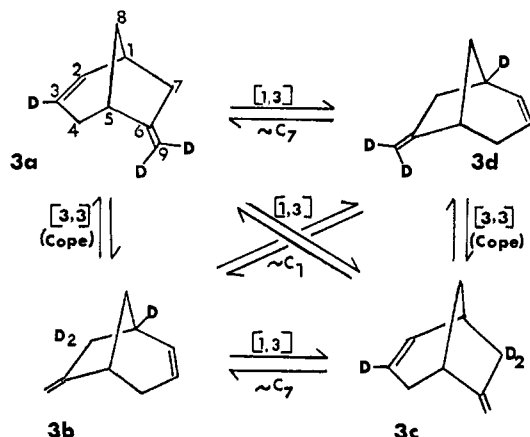


To follow the automerizations, which may be visualized *a priori* as interconversions of **3a**, **3b**, **3c**, and **3d** by any or all of the formal mechanisms shown, we note that the proton counts at C<sub>1</sub>, C<sub>3</sub>, C<sub>7</sub>, and C<sub>9</sub> respectively (corrected for full deuteration) in **3a** are 1, 0, 2, and 0, in **3b** are 0, 1, 0, and 2, in **3c** are 1, 0, 0, and 2, and in **3d** are 0, 1, 2, and 0. The rearrangements of the label at C<sub>3</sub> and at C<sub>9</sub> both are clean first-order reactions with rate constants<sup>6</sup> for approach to the equilibrium distribution, respectively,  $k_3 = (1.82 \pm 0.08) \times 10^{-5} \text{ sec}^{-1}$  and  $k_9 = (1.77 \pm 0.12) \times 10^{-5} \text{ sec}^{-1}$ .

If these rate constants are taken to be identical, only three formal mechanisms are possible (Scheme II):

Scheme II

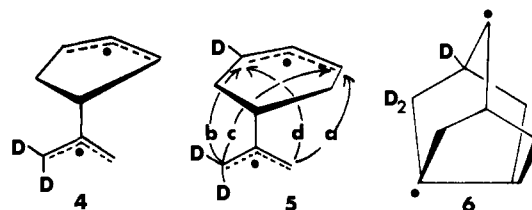


(4) **3a**  $\rightleftharpoons$  **3b** only (pure Cope rearrangement); (5) **3a**  $\rightleftharpoons$  equal amounts of **3c** + **3d** only; (6) any mixture of these two mechanisms. Category 6 includes as a special case the mixture one-third (4) and two-thirds (5), which is indistinguishable from a common randomized diradical intermediate. This species could arise from cleavage at C<sub>1</sub>-C<sub>7</sub> of **3a** and would recyclize with equal rates to **3a**, **3b**, **3c**, and **3d**.

Alternatively, on the (unjustified) assumption that the observed rate constant ratio of  $1.03 \pm 0.08$  is different from unity,  $k_3/k_9$  can be related to the rate constants for a mechanism involving competitive independent [1,3]-sigmatropy of C<sub>7</sub> (**3a**  $\rightarrow$  **3d**,  $k_8$ ) and randomized diradical formation ( $k_R$ ) by the equation  $1.03 = k_3/k_9 = 2(k_8/k_R) + 1$ , from which it may be calculated that  $k_8/k_R = 0.015$ . Thus, [1,3]-sigmatropy, if present at all, contributes only about one part in 70 to the overall rearrangement. The competitive mechanisms (1 and 2) above, which were compatible with the results in the **1a-b** system, cannot be important here.

What causes the apparent difference in behavior between **3a** and **1a-b**? It is conceivable that this merely reflects a shift, for some not very obvious reason, in the relative magnitudes of the competing rate constants in mechanisms 1 and 2. However, another formal possibility derives from mechanism 3, involving an "incompletely equilibrated" diradical. These species, **4**<sup>8</sup> from **1b** and **5** from **3a**, each are hypothetically derived by cleavage of the C<sub>1</sub>-C<sub>7</sub> bond and rotation of the exo-methylene group toward the underside of the remaining ring. Diradical **5** has a mirror plane, which

(6) Calculated using a nonweighted least-squares program kindly supplied by Professor K. B. Wiberg. An iterative procedure which varies the infinity value to give the best fit to the data gives values of  $1.67 \times 10^{-5}$  and  $1.65 \times 10^{-5} \text{ sec}^{-1}$ , respectively, for the two scrambling rate constants. The rates are not affected by glass wool.



requires two pairwise equivalences of the ring-closure rate constants,  $k_a = k_b$  and  $k_c = k_d$ . The pure Cope rearrangement of **3a**, mechanism 4, also might involve an intermediate 1,4-diradical<sup>7</sup> (**6**), which again would have C<sub>8</sub> symmetry. Either **5** or **6** necessarily would produce the equivalence of  $k_3$  and  $k_9$  observed here experimentally.

Distinctions among the mechanisms involving pure Cope rearrangement, randomized diradical, and symmetrical but "incompletely equilibrated" diradical are possible in principle in the **3a** system. One experimental approach involves optically active **3a**.

(7) Cf. (a) W. v. E. Doering, V. G. Toscano, and G. H. Beasley, *Tetrahedron*, **27**, 5299 (1971); (b) M. J. S. Dewar and L. E. Wade, *J. Amer. Chem. Soc.*, **95**, 290 (1973); (c) J. J. Gajewski, L. K. Hoffman, and C. N. Shih, *ibid.*, **96**, 3705 (1974).

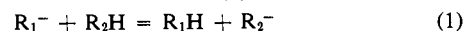
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Received June 14, 1974

### Intrinsic Acidities of Carbon Acids, RH, Bond Dissociation Energies of R-H, and Electron Affinities of R from Gas Phase Proton Transfer Equilibrium Measurements

Sir:

In recent years studies of gas phase acidities and basicities of organic compounds have led to valuable insights for the separation of intrinsic and solvent induced substituent effects.<sup>1-4</sup> The present study deals with carbon acids—a group which has been little investigated to date. Brauman<sup>1</sup> has observed that the acidity of toluene is comparable to methanol and ethanol. Bohme, *et al.*,<sup>5</sup> have ordered the acidities of 18 carbon acids between methane and nitromethane and revealed many interesting trends. However, since the compounds cover an energy range of 70 kcal/mol, little quantitative information may be extracted.

The acidities of 11 selected carbon acids, RH, measured in the present work are shown in Tables I and II. The data were obtained from measurement of the equilibrium constants  $K_1$  for the reaction (1) at 600°K. Using



$\Delta G^\circ_1 = -RT(\ln K_1)$  it was assumed that  $\Delta G^\circ_1 = \Delta H^\circ_1$  such that

$$\Delta G^\circ_1 = \Delta H^\circ_1 = D(R_2-H) - EA(R_2) - D(R_1-H) + EA(R_1)$$

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(3) M. Taagepera, W. G. Henderson, R. T. Brownlee, J. L. Beauchamp, D. Holtz, and R. W. Taft, *J. Amer. Chem. Soc.*, **94**, 1369 (1972).

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(5) D. K. Bohme, E. Lee Ruff, and L. B. Young, *J. Amer. Chem. Soc.*, **94**, 5153 (1972).

**Table I.** Gas Phase Acidities of RH, Bond Dissociation Energies  $D(\text{R}-\text{H})$ , and Electron Affinities,  $EA(\text{R})^a$ 

RH	$D(\text{R}-\text{H}) - EA(\text{R})^b$	$D(\text{R}-\text{H})$	$EA(\text{R})$
Cyclopentadiene	39.1	$81.2 \pm 1.2^9$	$42.4,^{10} 42.1$
1,4-Pentadiene	46.1	$68.5 \pm 2$	$22.4 \pm 2^c$
Diphenylmethane	$47.0 \pm 0.4$	$66.0 \pm 6^{12}$	$19.0 \pm 6$
Acetonitrile	$47.6 \pm 0.4$	$82.3 \pm 0.3^{12}$	$34.7 \pm 3.4$
Acetone	$50.1 \pm 0.4$	$98.0 \pm 2.6^{14}$	$47.9 \pm 3$
		$92.1^{15}$	42.0

<sup>a</sup> All values in kcal/mol. <sup>b</sup> May be made equal to proton affinity of  $\text{R}^-$  by adding  $I_p(\text{H}) = 313.6$  kcal/mol. <sup>c</sup> From theoretical calculation,<sup>11</sup> error assumed  $\pm 2$  kcal since calculation of  $EA(\text{benzyl})$  in same work differed by 2 kcal from experimental value.<sup>5</sup>

**Table II.** Gas Phase Acidities and Substituent Effects in Gas Phase Carbon Acids<sup>a</sup>

$\text{H}_2\text{C}-\text{H} (\sim 100)^b$	$\xrightarrow{33.1} \text{C}_6\text{H}_5\text{CH}_2-\text{H} (66.9)^5$	$\xrightarrow{19.9} (\text{C}_6\text{H}_5)_2\text{CH}-\text{H} (47.0)$
	$\xrightarrow{33.1} \text{C}_2\text{H}_5\text{CH}_2-\text{H} (66.9)^5$	$\xrightarrow{20.8} (\text{C}_2\text{H}_5)_2\text{CH}-\text{H} (46.1)$
	$\xrightarrow{49.4} \text{CH}_3\text{COCH}_2-\text{H} (50.1)$	$\xrightarrow{22.1} (\text{CH}_3\text{CO})_2\text{CH}-\text{H} (28)$
		$\xrightarrow{13.9} (\text{CH}_3\text{CO})(\text{C}_6\text{H}_5)\text{CH}-\text{H} (36.2)$
	$\xrightarrow{52.4} \text{CNCH}_2-\text{H} (47.6)$	$\xrightarrow{30.4} (\text{CN})_2\text{CH}-\text{H} (17.2)$
		$\xrightarrow{12.6} (\text{CN})(\text{C}_6\text{H}_5)\text{CH}-\text{H} (35)$
	$\xrightarrow{54.4} \text{C}_6\text{H}_5\text{COCH}_2-\text{H} (45.6)$	$\xrightarrow{21.4} (\text{C}_6\text{H}_5\text{CO})(\text{CH}_3\text{CO})\text{CH}-\text{H} (24.2)$

<sup>a</sup> Numbers in brackets correspond to  $(D - EA)$ , numbers over arrows correspond to change in  $(D - EA)$ , all values in kcal/mol. <sup>b</sup>  $EA(\text{CH}_3)$  not accurately known, assumed 5 kcal/mol.<sup>16</sup>

Acids whose  $D - EA$  had been determined previously<sup>4,6,7</sup> were used in equilibria with the unknown acids.<sup>8</sup> The assumption  $\Delta G_1 = \Delta H_1$ , i.e.,  $\Delta S_1 = 0$  is not rigorous. A  $\Delta S_1 < 2$  eu was found for proton transfer reactions measured previously.<sup>2,6,7</sup> A similarly low entropy change was also found in the present work for the pairs 1,4-pentadiene-pyrrole and acetylacetone-*o*- $\text{CH}_3$ , benzoic acid whose equilibria were examined in the range 240–330°. The apparatus and experimental techniques used are similar to those described in previous publications.<sup>6,7</sup>

Table I summarizes newly gained information on bond energies and electron affinities from  $(D - EA)$  determined in the present work.

The C–H bond energy in cyclopentadiene has been determined by Benson<sup>9</sup> as 81.2 kcal/mol. This value combined with the present  $(D - EA)$  of 39.1 kcal/mol leads to  $EA(\text{cyclopentadienyl}) = 42.1$  kcal/mol, which is in very good agreement with the  $EA$  of 42.4 kcal/mol determined directly by Brauman<sup>10</sup> using ICR photo-detachment.

Hoyland and Goodman<sup>11</sup> have calculated  $EA((\text{C}_2\text{H}_3)_2\text{CH}) = 22.4$  kcal/mol. Combined with the present  $(D - EA)$

of 46.1 kcal/mol this leads to  $D((\text{C}_2\text{H}_3)_2\text{CH}-\text{H}) = 68.5$  kcal/mol. This value is close to  $D((\text{C}_6\text{H}_5)_2\text{CH}-\text{H}) = 66$  kcal/mol<sup>12</sup> and agrees with the observation by Benson<sup>13</sup> that the stabilization of free radicals by a vicinal phenyl or vinyl group is nearly identical. The near identical acidities for divinylmethane and diphenylmethane observed in the present work follow logically the near identical acidities of propylene and toluene determined by Bohme.<sup>5</sup> Thus both the radical and carbanion experience stabilization by mono- or divinyl which is very similar to that caused by mono- or diphenyl substitution.

The C–H bond dissociation energies in acetone and

acetonitrile determined by Benson are 98.0<sup>14</sup> and 82.3 kcal/mol.<sup>12</sup> Combined with the present  $(D - EA)$  of 50.1 and 47.6 kcal/mol, they lead to  $EA(\text{CH}_3\text{COCH}_2) = 47.9$  and  $EA(\text{CNCH}_2) = 34.7$  kcal/mol. It is interesting to note that the bond dissociation energies of acetone and acetonitrile are dissimilar while the gas phase acidities are similar. The high  $D(\text{CH}_3\text{COCH}_2-\text{H})$  and the resulting high  $EA(\text{CH}_3\text{COCH}_2)$  mean that the acetyl group is ineffective for stabilization of the radical but very effective for the carbanion stabilization. This is in contrast with the cyano group which shows the more expected behavior of stabilizing both radical and anion. An earlier<sup>15</sup>  $D(\text{CH}_3\text{COCH}_2-\text{H}) = 92.1$  kcal/mol is lower and leads to some stabilization of the radical by the acetyl group.

The effects of substituents on the acidity of carbon acids are systematized in Table II. The compounds are shown as substituted methanes. The unsubstituted compound methane is included.<sup>16</sup> The substituents increase acidity in the order phenyl  $\approx$  vinyl  $<$  acetyl  $<$  CN  $<$  benzoyl. This order is similar to that observed in aqueous solution<sup>17</sup> where, however, CN  $<$  acetyl. The

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(8) The actual equilibria measured and the standard acids involved will be given in a future more comprehensive publication which will summarize results for carbon and nitrogen acids: T. B. McMahon and P. Kebarle, *J. Amer. Chem. Soc.*, to be submitted for publication.

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(14) R. K. Solly, D. M. Golden, and S. W. Benson, *Int. J. Chem. Kinet.*, **2**, 11 (1970).

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(16) V. I. Vedeneyev, L. V. Gurvich, V. N. Kondrat'yev, V. A. Medvedev, Ye. L. Frankevich, "Bond Energies, Ionization Potentials and Electron Affinities," Edward Arnold Publishers, London, 1966.

(17) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965.

table also shows that the increase of acidity by the second introduction of the same group is only some 60% of that by the first. Such attenuation with continued substitution is generally observed in the gas phase.<sup>1-4</sup> When the second substituent is different and more weakly acidifying than the first then the observed attenuation is larger. Thus introducing phenyl into acetylmethane leads to an acidity increase of 13.9 kcal/mol while introducing phenyl into the weaker acid phenylmethane leads to an increase of 19.9 kcal/mol. Similarly introducing phenyl into cyanomethane gives 12.6 kcal/mol which is also small compared to the 19.9 kcal/mol for introducing phenyl into phenylmethane. The introduction of acetyl into benzoylmethane leads to an acidity increase of 21.4 kcal/mol while acetyl into acetylmethane gives 22.1 kcal/mol. The difference in this case is smaller, a result that does not quite fit the trends mentioned above.

It is interesting to compare malononitrile, ( $D - EA$ ) = 17.2 kcal/mol, with the somewhat weaker chloroacetic acid, ( $D - EA$ ) = 19.6 kcal/mol.<sup>6</sup> In aqueous solution malononitrile<sup>17</sup> with a  $pK_a$  of 11.2 is drastically weaker than chloroacetic acid whose  $pK_a$  = 2.9. It follows that the acetate anion must be much more strongly hydrated than the carbanion even though the two anions are of similar size. The hydration difference should be due to two factors. Since carbon is not as electronegative as oxygen, acidity in carbon acids can be achieved only through charge dispersal by means of  $\sigma$ - and  $\pi$ -withdrawing groups. However, charge dispersal leads to low hydration interactions.<sup>18</sup> Secondly the carbanion has only one strong hydrogen bonding position, while the oxygen atom has two. The same two reasons to a greater or lesser degree make all carbon acids relatively much weaker in aqueous solution.

The acidities of the  $\beta$ -dicarbonyl compounds are further complicated by keto enol and tautomerism, steric effects, and dipole-dipole repulsions. The nature of these effects will be discussed in a future publication.<sup>8</sup>

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### Complexes of Benzyl Isocyanide with Ferrous Phthalocyanine. A Model for the Heme Group and a Solar Energy Storage System

Sir:

Although extensive studies of thermal and photochemical dissociation of alkyl isocyanides from hemoglobin and myoglobin have been reported,<sup>1-3</sup> studies of the reactions of alkylisocyanides with simple iron complexes which might reasonably serve as models for the heme group have been limited.<sup>4,5</sup> In previous papers we have reported on the kinetics and equilibria

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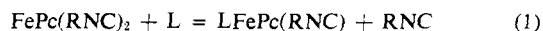
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(5) G. Condorelli, L. Giallongo, A. Giuffrida, and G. Romeo, *Inorg. Chim. Acta*, **7**, 7 (1973).

of carbon monoxide binding to iron porphyrin and phthalocyanine complexes in toluene solution.<sup>6,7</sup> While the iron porphyrins bind CO by a factor of  $10^5$  times better than the corresponding iron phthalocyanine complexes (in terms of the equilibrium  $L_2FeP + CO = LFeP(CO) + L$  where  $L$  = piperidine and  $P$  = protoporphyrin IX or phthalocyanine) the lability of the CO in the two systems is comparable and considerably greater than that reported for CO dissociation from iron glyoxime<sup>8</sup> or iron macrocycle systems.<sup>9</sup> In order to fully elucidate those features of the porphyrin ligand which gives rise to the unusual lability of ligands coordinated in axial positions,<sup>10,11</sup> we have extended our investigations to alkyl isocyanide ligands.

We report here on a markedly different lability of benzyl isocyanide (RNC) in the phthalocyanine (Pc) and porphyrin (P) systems and also on a novel photochemical dissociation of benzyl isocyanide which results in a reversible shift in an equilibrium due solely to light and a net storage of solar energy.

Addition of pyridine, piperidine, or methylimidazole to a toluene solution of (dibenzyl isocyanide)ferrous phthalocyanine ( $FePc(RNC)_2$ ),<sup>12</sup> results in a rapid reaction ( $k = 0.1 \text{ sec}^{-1}$  at  $20^\circ$ ) to give the monoisocyanide complex



Further reaction to give the diamine complex



is slow in the dark and is markedly dependent on the trans ligand L. Data for  $L$  = piperidine, pyridine, or methylimidazole show relative trans effects similar to those previously reported for CO dissociation from the analogous  $LFePc(CO)$  complexes (Table I). For each

**Table I.** Kinetic Data for Benzylisocyanide and Carbon Monoxide Dissociation from Ferrous Phthalocyanine Complexes in Toluene Solution

L trans	$k_{RNC},^a \text{ sec}^{-1}$	$k_{CO},^b \text{ sec}^{-1}$
Piperidine	$5.15 \times 10^{-4}$	0.13
Pyridine	$1.98 \times 10^{-4}$	0.09
Methylimidazole	$9.2 \times 10^{-5}$	0.02
Hemoglobin <sup>c</sup>	0.2	0.015

<sup>a</sup> This work,  $30^\circ$ . <sup>b</sup>  $23^\circ$ , ref 7. <sup>c</sup> For aqueous solutions,  $20^\circ$ , pH 7; from ref 1 p 276; RNC = ethylisocyanide.

of the ligands, L, the rate of benzyl isocyanide dissociation is a factor of  $\sim 10^3$  slower than the corresponding rate for CO. The large differences in RNC and CO lability stem from a similar difference in the stability constants.

Alkylisocyanides coordinated to hemoglobin or myoglobin or to free iron porphyrins do not display the inertness which is observed in the phthalocyanine sys-

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(12) Complete characterization of the compounds and the two equilibria (eq 1 and 2) will be reported.