the rate expression only when $k_{-1} >> k_2[\mathrm{HOAc}]$, *i.e.*, when C–O bond breaking is much faster than a proton transfer from O to O. Comparison of rate constants for typical C–O breaking processes

$$k_{\mathrm{obs}} = \frac{k_1k_2(K_w/K_a)[\mathrm{OAc}^-]}{k_{-1} + k_2[\mathrm{HOAc}]} \qquad (6)$$

and proton transfer processes from O to O is quite convincing evidence that k_{-1} cannot be larger than k_2. When k_2 is larger than k_{-1} eq. 6 becomes a specific base catalytic expression. Gold and Butler's mechanism and scheme C of the previous paragraph are discarded as mechanisms, leaving only scheme B to account for the catalytic effect of acetate toward acetic anhydride.

COMMUNICATIONS TO THE EDITOR

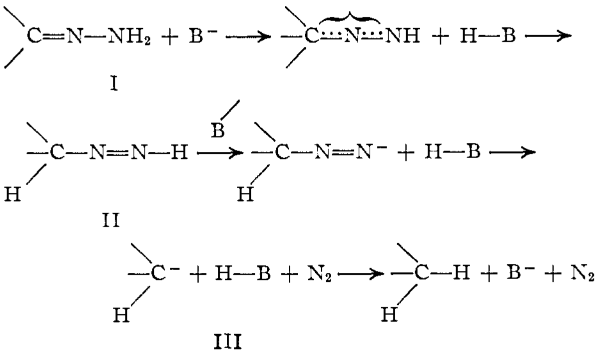
ROOM TEMPERATURE WOLFF-KISHNER REDUCTION AND COPE ELIMINATION REACTIONS[1]

Sir:

Evidence has accumulated that the reactivity of anions in dimethyl sulfoxide as solvent greatly exceeds that of hydroxylic solvents of comparable dielectric constant.[2] In the present work, we have found that use of dimethyl sulfoxide as solvent allows both the Wolff–Kishner reduction and the Cope elimination reactions to be run at room temperature.

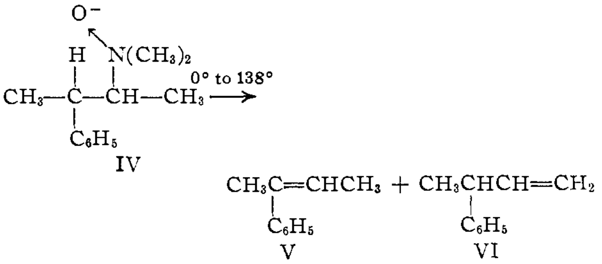
Slow addition of hydrazones of aldehydes and ketones to a solution of sublimed potassium *tert*-butoxide[3] in anhydrous dimethyl sulfoxide[2g] at 25° produced an immediate evolution of nitrogen and formation of hydrocarbon in 60–90% yields.[4] Typical yields of hydrocarbon obtained from the following starting materials are as given: benzophenone hydrazone, 90%; benzaldehyde hydrazone, 67%; camphor hydrazone, 64%; cyclohexanone hydrazone, 80%. The main by-product is azine, whose formation is favored by rapid addition of hydrazone to the reaction mixture.[5] The procedure as applied to benzophenone hydrazone is as follows. To a rapidly stirred mixture of 2 g. of sublimed potassium *tert*-butoxide[3] and 5 ml. of anhydrous dimethyl sulfoxide[2g] was added in very small portions over a 8-hour period 1.96 g. of benzophenone hydrazone. The solution turned deep red and nitrogen was evolved vigorously. The reaction mixture was shaken with a mixture of methylene chloride and water, and the organic layer was washed with water, dried and evaporated. Gross chromatography of the residue on alumina gave 1.5 g. of diphenylmethane and 0.2 g. of benzophenone azine. When an addition time of 0.5 hour was employed, the yield of diphenylmethane decreased to 72% and of azine increased to 22%.

In this reduction reaction, the rate-limiting step is probably a base-catalyzed isomerization of I to II, although proton abstraction from II to give III



undoubtedly is base catalyzed also. Apparently the activity of $\mathrm{RO^-}$ toward N–H is greatly enhanced in dimethyl sulfoxide for much the same reason that it is enhanced toward C—H.[2d,2g]

In most Cope elimination reactions, *tert*-amine oxides are pyrolyzed without solvent at temperatures of 120–150°.[6] Kinetics of the elimination reaction of *threo*- and *erythro*-N,N-dimethyl-3-phenyl-2-butylamine oxide (IV) to give *cis*- and *trans*-2-phenyl-2-butene (V) and 3-phenyl-1-butene (VI)[7] now have been studied in dimethyl sulfoxide–water mixtures, in tetrahydrofuran–water mixtures, and in the pure solvents. The reactions were followed by vapor phase chromatographic techniques which allowed the amounts of V and VI to be measured within ±1%. Within experimental



$$\mathrm{CH_3-C(H)(C_6H_5)-CH(N(CH_3)_2\rightarrow O^-)-CH_3} \xrightarrow{0^\circ \text{ to } 138^\circ} \mathrm{CH_3C(C_6H_5){=}CHCH_3} + \mathrm{CH_3CH(C_6H_5)CH{=}CH_2}$$

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[1] This work was supported by the Office of Ordnance Research, U. S. Army.

[2] (a) R. Fuchs and A. Nisbet, *J. Am. Chem. Soc.*, **81**, 2371 (1959); (b) R. A. Smiley and C. Arnold, *J. Org. Chem.*, **25**, 257 (1960); (c) L. Friedman and H. Shechter, *ibid.*, **25**, 877 (1960); (d) D. J. Cram, B. Rickborn and G. R. Knox, *J. Am. Chem. Soc.*, **82**, 6412 (1960); (e) J. Miller and A. J. Parker, *ibid.*, **83**, 117 (1961); (f) C. C. Price and W. H. Snyder, *ibid.*, **83**, 1773 (1961); (g) D. J. Cram, B. Rickborn, C. A. Kingsbury and P. Haberfield, *ibid.*, **83**, 3678 (1961).

[3] M. S. A. Research Corporation, Callery, Pa.

[4] With potassium hydroxide in ethylene glycol, this reaction requires 180–200° [D. Todd, "Organic Reactions," John Wiley and Sons, Inc., New York, Vol. 4, p. 378, 1948].

[5] In all cases, physical constants of starting materials, products and by-products check those of the literature.

[6] For example, A. C. Cope, C. L. Baumgardner and E. E. Schweizer, *J. Am. Chem. Soc.*, **79**, 4729 (1957).

[7] D. J. Cram and J. E. McCarty, *ibid.*, **76**, 5740 (1954).

error, production of V was completely stereospecific in all media. The value of the ratio of V to VI for *threo*-IV changed from 49 in pure dimethyl sulfoxide at 25° to 19 in tetrahydrofuran at 25° to 7 in water at 132°, whereas for *erythro*-IV the values with the corresponding solvents and temperatures were 16, 19 and 11. The reactions were cleanly first order in substrate. The reaction proceeded at a convenient rate *at 25° in dry dimethyl sulfoxide and tetrahydrofuran*[8] to give 80–90% yields of product, whereas temperatures of 132–138° were required in water, and yields were inferior due to polymerization of IV. Rate comparisons for *threo*-IV at 25° are (the rate in water at 25° had to be estimated by extrapolation from higher temperature): $k_{\mathrm{DMSO}}/k_{\mathrm{water}} \sim 10^5$; $k_{\mathrm{tetrahydrofuran}}/k_{\mathrm{water}} \sim 10^6$. For erythro-IV at 25°, the values were $k_{\mathrm{DMSO}}/k_{\mathrm{water}} \sim 10^4$; $k_{\mathrm{tetrahydrofuran}}/k_{\mathrm{water}} \sim 10^5$. For each isomer, addition of 10 mole % water to tetrahydrofuran depressed the rate by a factor of approximately 200, whereas similar treatment of dimethyl sulfoxide gave a decrease of only a factor of 5 to 10.

These data indicate that the activity of the negative oxygen of the amine oxide is subject to considerable variation, depending on whether it is hydrogen-bonded. The rate is higher in dry tetrahydrofuran than dry dimethyl sulfoxide because less solvation energy of the dipole has to be overcome in tetrahydrofuran in going to the transition state (charge is more dispersed in the transition state). The rate is higher in wet dimethyl sulfoxide than in wet tetrahydrofuran because unlike tetrahydrofuran, dimethyl sulfoxide acts as an internal drying agent, and competes with amine oxide for hydrogen bonds with the water present.

These results should find practical applications in synthetic and degradative chemistry in which low temperatures are required for the Wolff–Kishner or internal elimination reactions.

[8] Runs in anhydrous tetrahydrofuran and dimethyl sulfoxide were made by dissolving hydrated amine oxide in the dry solvent and drying out the water with Molecular Sieves (at 80° in the case of tetrahydrofuran).

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALIFORNIA
AT LOS ANGELES, LOS ANGELES
24, CALIFORNIA

DONALD J. CRAM
MELVILLE R. V. SAHYUN
GRAHAM R. KNOX

RECEIVED MARCH 9, 1962

SPECIES EQUILIBRIA IN NICKEL(II) PORPHYRIN SOLUTIONS: EFFECT OF PORPHYRIN STRUCTURE, SOLVENT AND TEMPERATURE[1]

Sir:

We wish to report our finding that nickel (II) porphyrins in basic solvents capable of acting as ligands (*e.g.*, pyridine and *n*-butylamine) can exist as an equilibrium mixture of two spectrally distinct species and that the relative concentrations of the two species are dependent upon porphyrin structure, solvent basicity, and temperature but, over the range of concentrations studied, are independent of nickel(II) porphyrin concentration.

Among the nickel(II) porphyrins that have been prepared from the metal-free porphyrin and nickel acetate in acetic acid solution, purified chromatographically, and crystallized out of chloroform-methanol are: Ni(II) mesoporphyrin IX dimethyl ester (Cpd. 1, m.p. 189°, *Anal.* Calcd. for $C_{36}H_{40}O_4N_4Ni$: C, 66.37; H, 6.05; N, 8.60. Found: C, 66.25; H, 6.40; N, 8.61), Ni(II) deuteroporphyrin IX dimethyl ester (Cpd. 2, m.p. 202°, *Anal.* Calcd. for $C_{32}H_{32}O_4N_4Ni$: C, 64.56; H, 5.42; N, 9.41. Found: C, 64.75, 64.55; H, 5.56, 5.60; N, 9.36, 9.66), Ni(II) 2,4-bis-(2-carboxycyclopropyl)-deuteroporphyrin IX, 2,4-diethyl ester 6,7-dimethyl ester (Cpd. 3, m.p. 99–101°, *Anal.* Calcd. for $C_{44}H_{48}N_4O_8Ni$: C, 64.41; H, 5.90; N, 6.38. Found: C, 64.19; H, 6.05; N, 7.02). Ni(II) 2,4-diacetyldeuteroporphyrin IX dimethyl ester (Cpd. 4, m.p. 204–205°, *Anal.* Calcd. for $C_{36}H_{36}O_6N_4Ni$: C, 63.64; H, 5.34; N, 8.64. Found: C, 63.79; H, 5.58; N, 8.31; Ni, 8.55), and Ni(II) 2,4-diformyldeuteroporphyrin IX dimethyl ester (Cpd. 5, m.p. 270°, *Anal.* Calcd. for $C_{34}H_{32}N_4O_6Ni$: C, 62.70; H, 4.95; N, 8.60. Found: C, 62.37; H, 5.24; N, 8.57).

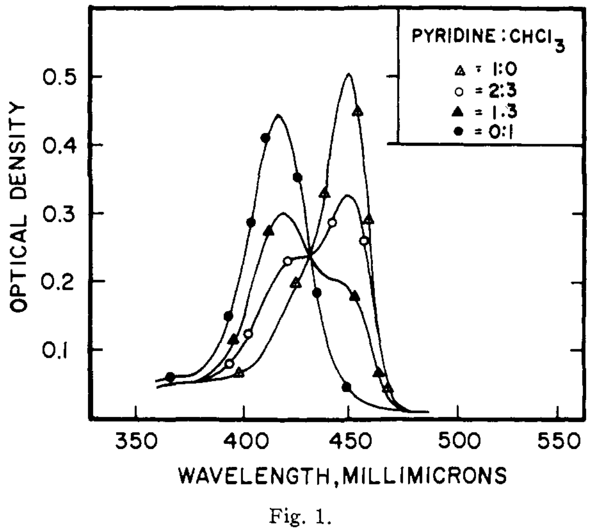

Fig. 1.

The spectrum of a given nickel(II) porphyrin in solution can differ with solvent and temperature. As shown in Fig. 1 for Cpd. 4 ($2.0 \times 10^{-6}M$) in pyridine–chloroform mixtures (v./v.) at 30°, these spectra are characterized by isosbestic points indicative of an equilibrium between two, and only two, species. In solvents of low basicity (*e.g.*, chloroform, benzene, 1,2-dichloroethane and dioxane) only one species (I) is observed; in more basic solvents a second species (II) appears whose spectrum has a Soret band maximum at about 30 mμ longer wave length and other differences. The D_{II}/D_I values[2] for Cpd. 2 ($2.0 \times 10^{-5}M$) at 30° are 0.05, 0.09, 0.19, 0.62 and 2.33 in chloroform, pyridine–water (1:1), pyridine–chloroform (1:1), pyridine and *n*-butylamine, respectively. The lower is the temperature the greater is the relative amount of Species II present. In pyridine, Cpd. 2 ($3.7 \times 10^{-5}M$) exhibits D_{II}/D_I values of 0.62, 0.93 and 1.44 at 30°, 20° and 10°, respectively; for Cpd. 4 ($5.7 \times 10^{-5}M$), D_{II}/D_I is 1.0 at 83° and 3.0 at 30°.

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[1] Presented in part at the 138th National Meeting, American Chemical Society, New York, N. Y., 1960.

[2] D_I and D_{II} represent optical densities at Soret band maxima of Species I and Species II, respectively.