

Fig. 3.—First-order dependence on nitric oxide for constant oxygen.

based on the absorption frequency. Nitric oxide contains a non-bonding electron, and its absorption maximum is only slightly shifted by bond formation, for example

Species	ω (cm. ⁻¹)	Ref.
NO	1876	
F-NO	1845	1
OO-NO	1840	(This work)
O ₂ N-NO	1830	2
Cl-NO	1800	3

A vibrational analysis of the symmetrical nitrate radical, with a reasonable assignment of force constants, indicates that the infrared active frequencies should be about 664 cm.⁻¹, 904 cm.⁻¹ and 1603 cm.⁻¹, none anywhere near the observed band at 1840 cm.⁻¹.

If one assumes that the Beer's law constant for OONO is the same as for N₂O₃ and if the entropy is estimated to be 68 cal./deg.-mole, the heat of reaction 3 is about -6 kcal./mole, and the equilibrium constant at 25° is about 3.4 × 10⁻³ atm.⁻¹. On the other hand, if one assumes the Beer's law constant for OONO to be the same as that for NO, then the heat of reaction 3 is about -9 kcal./mole, and the equilibrium constant at 25° is about 3.2 × 10⁻¹ atm.⁻¹. The true situation is probably somewhere between these two limits.

This work is believed to have significance with respect to the mechanism of nitric oxide oxidation and with respect to the role of nitric oxide as an oxidizing agent when it is in the atmosphere in trace amounts.

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(1) P. J. H. Wolty, E. A. Jones and A. H. Nielsen, *J. Chem. Phys.*, **20**, 378 (1952).

(2) L. D'Or and P. Tarte, *Bull. soc. roy. sci. Liege*, **23**, 276 (1953).

(3) W. G. Burns and H. J. Bernstein, *J. Chem. Phys.*, **18**, 1669 (1950).

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THE HYDROXYMETHYLENE KETONE-ALDO ENOL EQUILIBRIUM

Sir:

The enolization of β -keto aldehydes (I) may lead to two possible tautomeric enols: aldo enol (I_a) and hydroxymethylene ketone (I_b). The long-standing supposition that the hydroxymethylene ketone is the predominant if not the exclusive enol form at equilib-

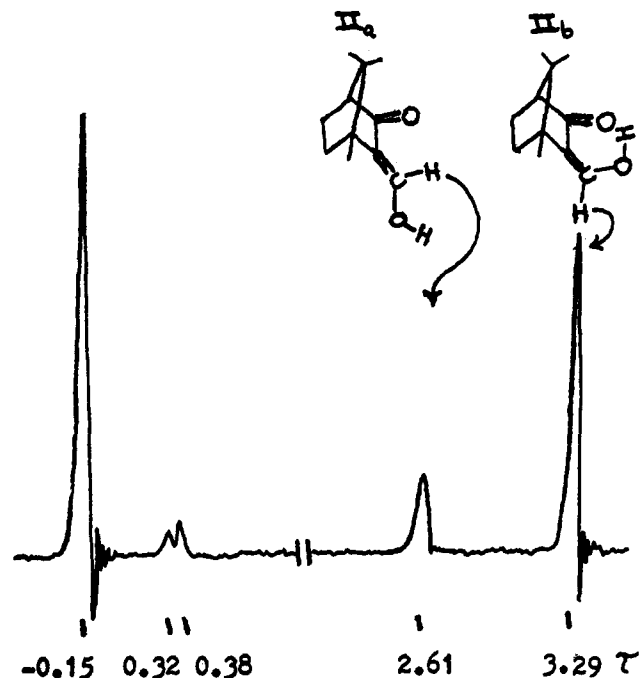
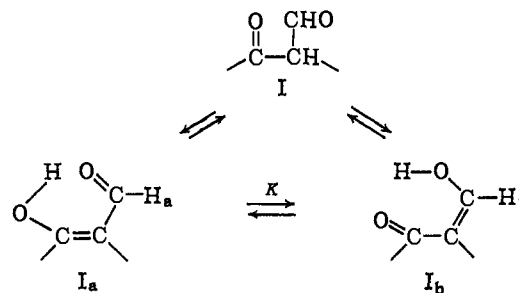


Fig. 1.—The low field part of the proton magnetic resonance spectrum of 3-formylcamphor (II).

rium apparently arises largely from the demonstration by Claisen nearly 70 years ago that 3-formylcamphor (II, no. 12) underwent numerous reactions each consistent with that anticipated for 3-hydroxymethylene-camphor.¹ Reactions of β -keto aldehydes, however, do not necessarily reflect the composition of their tautomeric equilibria.



The direction of enolization of a number of cyclic β -keto aldehydes has been estimated by n.m.r. spectroscopy. The equilibria between I and I_a, I_b are expected to be slow with regard to spectra averaging,² and the equilibrium between I_a and I_b fast.³ Consequently, the recorded spectrum should show unenolized I and a weighted average of enols I_a and I_b. From the observed averaged chemical shift of H_a and H_b (δ^0), the mole fraction of I_b at equilibrium is given by: $N_{I_b} = (\delta^0 - \delta_a) / (\delta_b - \delta_a)$ where δ_a and δ_b are the chemical shifts of H_a and H_b, respectively. Taking the δ of the aldehyde proton of salicylaldehyde (0.18 τ) and adding 0.61 p.p.m., the deshielding arising from the anisotropy of the benzene ring⁴ (assuming a planar molecule and standard bond lengths and angles), a value of 0.79 τ is obtained for δ_a . The n.m.r. spectrum of 3-formylcamphor (II) was measured with the

(1) L. Claisen, *Ann.*, **281**, 306 (1894); A. W. Bishop, L. Claisen and W. Sinclair, *ibid.*, **281**, 314 (1894).

(2) J. A. Pople, W. G. Schneider and H. S. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., New York, N. Y., 1959, chapter 17.

(3) The small change in the equilibrium position of the enol proton is undoubtedly a low activation energy process.

(4) Estimated from the tables of C. E. Johnson, Jr., and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958).

TABLE I^a
THE DIRECTION OF ENOLIZATION OF α -FORMYL CYCLIC KETONES

No.	Ketone	δ^0 (τ) ^b	K	(% Ib)	No.	Ketone	δ^0 (τ) ^b	K	(% Ib)
1	Cyclopentanone	2.73	3.54	78	7	Cyclododecanone	1.49	0.39	28
2	Cyclohexanone	1.39	0.32	24	8	2-Isopropylcyclohexanone	1.49	.39	28
3	Cycloheptanone	2.43	1.94	66	9	4,4-Dimethyl-2-cyclohexenone	2.57	2.45	71
4	Cyclooctanone	1.89	0.79	44	10	2-Benzal-4- <i>t</i> -butylcyclohexanone	1.05	0.11	10
5	Cyclononanone	1.57	.45	31	11	Bicyclo[2:2:2]octanone	2.98	7.34	88
6	Cyclodecanone	1.24	.22	18	12	Camphor	3.29		100

^a All measurements were made on 10% solutions (by weight) in carbon tetrachloride at $25 \pm 1^\circ$ and at 40 Mc. ^b ± 0.01 p.p.m.

expectation that the high strain in the internal double bond of Ia would provide the impetus for the exclusive preference for Ib. The low field part of the n.m.r. spectrum of II is shown in Fig. 1. The signal at -0.15τ is assigned to the hydroxyl proton (disappears upon deuterium exchange) and the doublet at 0.32 and 0.38 τ is assigned to the *exo*- and *endo*- non-enolized (6%) aldehyde proton (splitting remains upon α -hydrogen deuterium exchange). The absorptions at 2.61 and 3.29 τ have a total area equal to that of the hydroxyl absorption. The relative absorption area $2.61/3.29 \tau$ increases from 5/95 for a 10% to 31/69 for a 26% solution (by weight) of II in CCl_4 to 78/22 for a 14% solution of II in CCl_4 containing 8% dimethyl sulfoxide.⁵ The absorptions at 2.61 and 3.29 τ are consequently assigned to the vinyl proton of IIa and IIb, respectively. The separation between these absorptions (0.68 p.p.m.) is comparable to the separation between the vinyl protons of 2-methylenecycloalkanes.⁶ The value of 3.29 τ now may be assigned to δ_b . Using the experimental values for δ_a and δ_b , the percentage of Ib and the equilibrium constant, *K*, were estimated for a series of cyclic β -keto aldehydes at 25° . These data are given in Table I. The β -keto aldehydes were found to be >99% enolized except for no. 1 (89% enol), no. 11 (98% enol), and no. 12. For several of the enols, H_b , O-H proton spin coupling was observed at 25° . This coupling was determined for the other enols at reduced temperatures.⁷ A plot of this coupling as a function of the percentage of Ib is shown in Fig. 2. The linear relationship and the intercept of near zero coupling substantiate the reliability of the models employed and the derived equilibrium constants. It is of interest that the only slight deviation from the line of the point for II (no. 12) in Fig. 2 suggests that the magnitude of this coupling is not strongly dependent upon the strength of the hydrogen bond.⁸

The data in Table I clearly show that the direction of enolization of cyclic β -keto aldehydes is strongly dependent upon structure. The trends (excluding no. 9 and 10) may be rationalized in terms of π -strain (the strain in double bonds). Further details of this work (including acyclic systems) will be discussed soon.⁹

(5) Intermolecular hydrogen bonded enol forms of I were not observed for the other systems investigated.

(6) Unpublished results from this Laboratory. See also L. M. Jackman, "Nuclear Magnetic Resonance Spectroscopy," Pergamon Press, New York, N. Y., 1959, p. 123.

(7) The observed coupling is a weighted average of the contributions from Ia and Ib. At temperatures below 25° , 10% solutions in carbon disulfide were used. There were no effects on chemical shifts upon changing to this solvent.

(8) The chemical shifts of the enol protons ranged between -0.15 (no. 12) and -5.15τ (no. 7).

(9) NOTE ADDED IN PROOF.—The n.m.r. study of α -formyl ketones by Forsén and Nilsson [*Arkiv Kemi*, **19**, 569 (1962); **20**, 41 (1963)] has been noticed. They report proton spin coupling between H_b , O-H for several acyclic derivatives and erroneously consider that this coupling should vanish upon rapid intramolecular O-H exchange (Ia, Ib equilibrium fast). When this coupling was observed, the exchange was considered slow and since, in these instances, no absorption representative of the aldo enol form was seen, the formyl ketone was thought to exist in the hydroxymethylene form. For no. 2, no such coupling was observed and they somehow reasoned that this material exists in the aldo enol form (in qualitative agreement with results

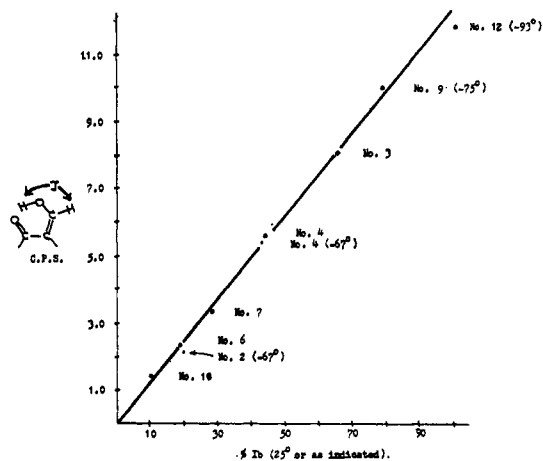


Figure 2.

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presented here). Nuclear spin state averaging resulting from rapid proton exchange should occur only for the intermolecular process.

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D-ribo-HEXOS-3-ULOSE, A NEW DICARBONYL-SUGAR^{1,2} Sir:

A new crystalline disaccharide was isolated recently from culture media of the crown-gall tumor-inducing organism *Agrobacterium tumefaciens* grown on sucrose as the carbon source.³ It was characterized by a variety of physical, chemical and enzymatic techniques and evidence has been presented to prove the structure of the new keto compound to be α -D-ribo-hexopyranosyl-3-ulose β -D-fructofuranoside (referred to below as "3-ketosucrose"). When the conversion of sucrose to 3-ketosucrose was first reported,⁴ D-fructose was the only product identified following hydrolysis with acid or enzyme. When crystalline 3-ketosucrose became available,³ hydrolysis in 0.05 N H_2SO_4 or with β -D-fructofuranoside fructohydrolase (3.2.1.26)⁵ resulted in the identification of two products, one of which was identical chromatographically with fructose while the other gave a deep red color with urea phosphate⁶ and

(1) Issued as Microbiology Research Institute No. 557.

(2) The new sugar was named in accordance with the "Rules of Carbohydrate Nomenclature," published by the American Chemical Society, see *J. Org. Chem.*, **28**, 251 (1963).

(3) S. Fukui, R. M. Hochster, R. Durbin, E. E. Grebner and D. S. Feingold, *Bull. Res. Council Israel*, **11A4** (Hestrin Memorial Issue), 262 (1963).

(4) D. S. Feingold, R. Durbin and E. E. Grebner, Abstracts of the 140th National Meeting of the American Chemical Society, 1961, p. 3D.

(5) Usage as recommended by the Commission on Enzymes of the International Union of Biochemistry, 1961.

(6) C. S. Wise, R. J. Dimler, H. A. Davis and C. E. Rist, *Anal. Chem.*, **27**, 33 (1955).