TABLE I

KETENE ACETYLATION PRODUCTS OF IMIDES

Imide Employed	Solvent	Catalyst	Appearance of Acetylated Product	M.P., °C.	Yield, %	Nitrogen, % Theor.	Nitrogen, % Exptl.
Acetanilide[a]	CCl_4	H_2SO_4	White crystals	38[b]	76	7.91	7.65
Naphthalimide	$C_2H_5OC_2H_5$	AcONa	Pink crystals	275–277(dec.)	57	5.86	5.98
4-Nitrophthalimide	CCl_4	AcONa	Yellow crystals	105–107	22	11.96	11.67
Phthalimide	CCl_4	AcONa	Butter-scotch crystals	128–130[c]	18	7.41	7.30
Pyromelliticdiimide	C_6H_6	AcONa	Tan crystals	138–140(dec.)	50	9.34	9.31
Saccharin	C_6H_6	AcONa	White crystals	196–200(dec.)[d]	70	6.23	6.25
Succinimide	hot CCl_4	AcONa	Yellow crystals	38[e]	51	9.93	9.82
Tetrahydrophthalimide	CCl_4	AcONa	White crystals	123–124	27	7.26	7.23

[a] Not an imide but an *N*-phenyl amide. [b] J. J. Sudborough, *J. Chem. Soc.*, 533 (1901), reports a m.p. of 37°. [c] T. W. Evans and W. M. Dehn, *J. Am. Chem. Soc.*, 51, 3651 (1929), reports a m.p. of 135–136°. [d] A mixed melting point also. [e] C. Djerassi and C. T. Lenk, *J. Am. Chem. Soc.*, 75, 3493 (1953), reports a m.p. of 40–41°.

was then mixed with the compound to be acetylated in an absorption apparatus[6] that had been previously designed in our laboratories. The compound being acetylated was dissolved in a suitable solvent placed in the absorption apparatus.

The imides for this study were all suspended in carbon tetrachloride, benzene, or ethyl ether at room temperature, with the exception of succinimide, which was suspended in hot carbon tetrachloride. A common catalyst found to be effective with all the imides acetylated was sodium acetate. The imide was weighed out in a 0.03-mole quantity. This, together with 0.03 grams of catalyst, was added to an 80-ml. portion of the solvent in the absorption flask. Ketene was passed through the reaction mixture until an equivalent molar amount had been added. A slight excess was added to ensure complete reaction. After the addition was complete, the mixture was separated from any residue which failed to dissolve. This residue was found in each case to be traces of unreacted parent compound and was, therefore, discarded. The mixture was then cooled and the acetylated imide crystallized out in surprisingly pure form.

All acetylated imides were verified and identified by mixed melting points with samples of the same compounds prepared by other approved means, or by micro-Kjeldahl and micro-Dumas nitrogen determinations.

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[6] A. N. Bolstad and R. E. Dunbar, *Ind. Eng. Chem., Anal. Ed.*, 18, 337 (1946).

The Structure of Amidoximes[1]

H. E. UNGNADE AND L. W. KISSINGER

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Amidoximes result primarily from the action of hydroxylamine on cyanides or the amination of hydroxamic acid chlorides with amines or ammonia. Neither the method of synthesis nor the reactions, however, permit a distinction between the isomeric structures Ia and Ib.

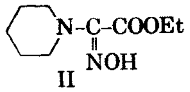

$\mathrm{R\underset{\substack{\| \\ NH}}{C}NHOH}$

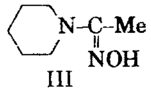
Ia


$\mathrm{R\underset{\substack{\| \\ NOH}}{C}NH_2}$

Ib

For this purpose the infrared absorption spectra of a few selected amidoximes have been compared with those of authentic oximino compounds of similar structure and with amidoximes derived from secondary amines (II and III) which can only possess structures corresponding to Ib.


II


III

A recent investigation of a series of amidoximes has described infrared absorption bands for these compounds which were assigned to NH stretching, OH stretching, NH deformation, C=N stretching, and N—O stretching.[2]

Similar bands have been observed in the present investigation (Table I). The broad bands in the region of 3.04–3.22 μ are probably due to associated NH and OH. They are much weaker in dilute solutions while the monomer bands at 2.80–2.93 μ are increased in intensity.

Strong bands at 5.95–6.24 μ are assigned to C=N stretching. Theoretical considerations permit the

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[1] This work was performed under the auspices of the U. S. Atomic Energy Commission.

[2] J. Barrans, R. Mathis-Noël, and F. Mathis, *Compt. rend.*, 245, 419 (1957).

TABLE I

INFRARED ABSORPTION SPECTRA OF AMIDOXIMES AND OTHER OXIMINO COMPOUNDS

Compounds	OH	OH	C=O	C=N	C—O—C	
		Amidoximes				
HN=CHNHOH	2.89	3.20[a]	..	5.95[b]	..	[c]
HONH—C(=NH)COOEt	2.88	3.16[a]	5.80	6.01[d]	8.19	[e]
III	2.84	3.12	..	6.17	..	[e]
II	2.81	3.09	5.77	6.21	8.16	[e]
		Oximino Acids				
$CH_3C(=NOH)COOH$	..	3.04	5.78	6.15	..	[c]
$C_2H_5C(=NOH)COOH$	..	3.04	5.78	6.14	..	[c]
N≡CC(=NOH)COOH	2.92	3.22	5.74	6.15	..	[c]
		Oximino Esters				
HON=CHCOOEt	2.84	3.04	5.79	6.14	8.00	[e]
$CH_3C(=NOH)COOEt$	2.85[sh]	3.12	5.82	6.16	8.75	[e]
$C_2H_5C(=NOH)COOEt$	2.82	3.10	5.81	6.16	8.70	[e]
HON=CClCOOEt	2.86[sh]	3.06	5.75	6.24	7.81	[e]
N≡CC(=NOH)COOEt	2.86	3.12	5.75	6.24	7.74	[e]
$CH_3COC(=NOH)COOEt$	2.83	3.16	5.73	6.14	8.15	[e]

[a] Probably combined OH and NH absorption. [b] In KBr (0.5%) the C=N band occurred at 5.96 μ. [c] 2% solution in acetonitrile. [d] In KBr (0.5%) the C=N band was found at 5.99 μ. [e] 5% solution in chloroform. *sh* = shoulder.

TABLE II

INFRARED ABSORPTION SPECTRA OF ETHYL AMINO-OXIMINOACETATE

Compounds	Solvent[a]	OH	OH[b]	C=O	C=N	NH	C—O—C
Hydrochloride	MeCN	[c]	3.18	5.65	5.85	6.21	8.08
Ester	MeCN	2.96	[c]	5.78	6.02	6.36	8.16
Ester	KBr[d]	2.89	3.18	5.80	5.99	6.37	8.11
Ester	$CHCl_3$	2.88	3.16	5.80	6.01	6.41	8.19
Ester	MeOH	[c]	[c]	5.78	6.04	6.40	8.30
Ester	$(CH_2)_5NH$	2.93	3.09	5.80	6.04	6.35	8.33
Sodium salt	KBr[d]	[c]	[c]	5.86	6.20	6.40	8.26

[a] Determined in concentrations of 5 and 10%. [b] Probably combined OH and NH absorption. [c] These bands could not be observed. [d] Potassium bromide pressing, 0.5 mm. thick, concentration 0.5%.

conclusion that the C=N frequency for C=NH compounds will be found at values about 40 cm.$^{-1}$ higher than that for similarly constituted C=NOH compounds.[3] The results show that oximino compounds including the amidoximes II and III have C=N stretching bands at 6.14–6.24 μ. Formamidoxime, ethyl amino-oximinoacetate (I, R=H and COOEt), and a series of other amidoximes (I, R = alkyl and aryl),[2] however, absorb at 5.95–6.02 μ, *i.e.* approximately at the predicted wave length for C=NH compounds both in neutral solution and in the solid state.

The formation of the sodium salt of ethyl amino-oximinoacetate by reaction with sodium alkoxides is accompanied by a shift of the C=N stretching band from 6.01 to 6.20 μ (Table II), corresponding to an isomerization from the imino structure Ia to the oximino structure Ib, presumably due to the greater acidity of the latter. In neutral or acid solvents, in piperidine, and in the solid state the C=N band for this ester is found at values below 6.05 μ and the compound is best represented by the imino structure Ia. The assignments of the C=N frequencies are in agreement with the literature values.[4]

Unsubstituted amidoximes I (a or b) have NH deformation bands of medium intensity at 6.2–6.4 μ (see also ref. 2) which must be absent in amidoximes corresponding to structures II and III. Absorption bands at 10.50–10.87 μ, assigned to N—O stretching,[2,5] occur in all amidoximes which have been examined.

It may be concluded that the infrared evidence favors the imino structure Ia rather than the oximino structure for the unsubstituted amidoximes except in strongly basic solutions.

Subject to the usual limitations of deducing structure from reactions, this conclusion is further indicated by the action of formaldehyde on amidoximes. Ethyl amino-oximinoacetate (I, R = COOEt) fails to react to any appreciable extent with formaldehyde in aqueous solution. Formamidoxime (I, R = H), on the other hand, gives a good yield of a

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[3] Calculations from force constants by E. Dan Loughran, Los Alamos Scientific Laboratory.

[4] S. Califano and W. Lüttke, *Z. physik. Chem., N.F.*, **5**, 240 (1955); **6**, 83 (1956); J. Fabian, M. Legrand, and P. Poirier, *Bull. soc. chim. France*, **10**, 1499 (1956); G. Duyckaerts, *Bull. soc. roy. sci. Liege*, **21**, 196 (1952).

[5] A. Palm and H. Werbin, *Can. J. Chem.*, **32**, 858 (1954).

crystalline alcohol, which is stable at 0° but is gradually dehydrated at 25°. The dehydration can be accelerated in boiling benzene and the formed water removed as benzene azeotrope. The dehydration product is a polymer rather than a trimethylenetriamine derivative which is the expected product if formaldehyde reacts with the amide nitrogen of structure Ib.

Compounds II and III have been prepared by amination of the respective hydroxamic acid chlorides with piperidine.

EXPERIMENTAL[6]

Formamidoxime, ethyl amino-oximinoacetate, α-oximino esters, and α-oximino acids were prepared according to literature methods. It was found, however, that ethyl amino-oximinoacetate could be prepared much more easily by amination of ethyl chloro-oximinoacetate.

Ethyl amino-oximinoacetate. Ethyl chloro-oximinoacetate (1.0 g., 0.0066 mole), dissolved in 50 ml. of dry ether, was treated with dry ammonia gas at 0°. The precipitated ammonium chloride was filtered with suction and the filtrate was evaporated under reduced pressure. The crystalline residue, m.p. 97–98°, weighed 0.51 g. (58%) and did not depress the melting point of authentic material.

The *sodium salt* was obtained as a yellow solid in 97% yield by evaporating an ethanol solution of the ester (0.002 mole) and sodium ethoxide (0.002 mole) in a high vacuum at room temperature.

Anal. Calcd. for $C_4H_7N_2NaO_3$: Na, 14.92. Found: Na, 15.08.

Ethyl piperidino-oximinoacetate (II). Ethyl chloro-oximinoacetate (2.0 g., 0.014 mole) in 100 ml. of dry ether was treated with shaking at 0° with a solution of piperidine (2.4 g., 0.028 mole) in 50 ml. of ether. The precipitated hydrochloride was filtered after 0.5 hr. at 0° and 1.5 hr. at 25° and the filtrate was evaporated under reduced pressure. The pale yellow oil (2.7 g., 96%) was distilled from a molecular still and boiled at 120° (0.05 mm.), n_D^{25} 1.5042, yield 1.26 g.

Anal. Calcd. for $C_9H_{16}N_2O_3$: C, 53.99; H, 8.05; N, 14.00. Found: C, 54.60; H, 8.13; N, 13.79.

Hydroxymethylformamidoxime. Formamidoxime (3.0 g., 0.05 mole) was dissolved in 5 ml. of water and 5 ml. of 95% ethanol. To this solution was added with stirring formalin (5 ml., 0.06 mole) and the warm mixture was cooled to 0°. The solid mass was diluted with an equal volume of 95% ethanol, filtered, washed with ethanol and ether, and dried, yielding 2.8 g. (62%), m.p. 102–103° (dec.), λ(C=N) 5.95 μ, λ(NH def.) 6.31 μ. OH, NH, and CH stretching bands were not resolved in KBr.

Anal. Calcd. for $C_2H_6N_2O_2$: C, 26.67; H, 6.71; N, 31.11. Found: C, 26.26, 26.24; H, 6.74, 6.67; N, 31.07.

The solid alcohol was stable at 0° but liquefied on standing at room temperature over a period of several weeks. The infrared spectrum of the product was identical with that of the polymer below.

Poly(methyleneformamidoxime). Hydroxymethylformamidoxime (0.53 g., 0.0059 mole) was suspended in 25 ml. of benzene and refluxed over a water trap for 24 hr. A red insoluble resin separated from solution and a drop of water collected in the trap. The resin weighed 0.42 g. (98%) and had broad bands in the infrared at 3.15 μ (OH), 6.01 μ (C=N), and 13.0 μ. It was insoluble in acetone (suggesting cross-linking), benzene, and chloroform.

Anal. Calcd. for $C_2H_4N_2O$: C, 33.32; H, 5.59; N, 38.89. Found: C, 32.87, 33.56; H, 6.84, 6.72; N, 38.83, 39.39.

Infrared absorption spectra were determined with a Perkin-Elmer Model 21 spectrophotometer with sodium chloride prisms in matched cells of 0.1-mm. path length for solutions and in KBr pellets of 0.5-mm. thickness for solids.

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[6] Microanalyses by M. J. Naranjo. All temperatures are uncorrected.

Mechanism of Reduction of Alkylmercuric Salts with Sodium Stannite

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Three methods generally employed to reduce alkylmercuric salts to dialkylmercury compounds are the following:

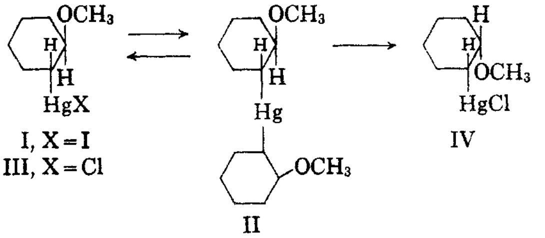
$$2\ RHgX \longrightarrow R_2Hg$$

1. N_2H_4
2. $Na_2S_2O_3$
3. Na_2SnO_2

The first has been shown to result in racemization about the carbon-mercury bond, suggesting formation of free radical intermediates.[1,2] The second method, applied to 3-bromomercuricamphor,[2] gives rise to retention of configuration, suggesting an SE2 mechanism.[3] Using the third method, Sand[4] isolated an intermediate mercurous compound RHgHgR which decomposed to R_2Hg on heating. For this transformation of the mercurous intermediate to R_2Hg and mercury one can visualize either some type of rearrangement process involving retention of configuration or a free radical mechanism permitting racemization, such as the following:

$$RHgHgR \longrightarrow RHg\cdot + Hg + R\cdot$$
$$RHg\cdot + R\cdot \longrightarrow RHgR$$

In this connection the reduction of *trans*-2-methoxycyclohexylmercuric iodide (I) is of interest.



I, X=I
III, X=Cl
II
IV

trans-2-Methoxycyclohexylmercuric iodide (I) was reduced to a dialkylmercury II, which was not examined directly, but was converted with mercuric

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(1) G. F Wright, *Can. J. Chem.*, **30**, 268 (1952).

(2) O. A. Reutov and Tsin-Chzhu Lu, *Doklady. Akad. Nauk. S.S.S.R.*, **110**, 575 (1956); *Chem. Abstr.*, **51**, 8042 (1957).

(3) S. Winstein, T. G. Traylor, and C. S. Garner, *J. Am. Chem. Soc.*, **77**, 3741 (1955).

(4) J. Sand, *Ber.*, **34**, 2913 (1901).