scribed by Fox and Chrisman[8] for liquids of high density and low surface tension.

The difference in surface tension between a fluorinated diester and its hydrogen-containing analog is illustrated by diethyl octafluoroadipate (22.7 dynes/cm.) and diethyl adipate (28.0 dynes/cm.). This difference is comparable to that observed for fluorocarbons and hydrocarbons. It will also be noted that, with the exception of *m*-trifluoromethylbenzyl heptafluorobutyrate,[9] the surface tension generally decreases with increasing fluorine content. A corollary to this observation may be drawn by noting the effect of increasing numbers of $-CF_2$ groups. While the addition of a methylene group is normally attended by an increase in surface tension (as illustrated by 1,5-pentanediol diheptafluorobutyrate and the corresponding 1,6-hexanediol ester), the value is lowered by the addition of $-CF_2$ groups, though this decrease becomes much smaller with increasing length of the fluorinated chain. This may be seen in the homologous series, $CF_3CO_2(CH_2)_5O_2CCF_3$, $C_3F_7CO_2(CH_2)_5O_2CC_3F_7$ and $C_7F_{15}CO_2(CH_2)_5O_2CC_7F_{15}$. Similar results were reported by Schulman and Zisman.[5]

In Table II are listed the experimental parachors of a few of these compounds, which were calculated from the surface tensions by the Sugden equation.[10] These values are compared with those calculated from the atomic and structural constants of Sugden[10] and of Mumford and Phillips.[11]

TABLE II

PARACHOR DATA

Compound	Calcd. parachor Sugden	M.p.,°C.[11]	Expl. parachor	P_F
$C_2H_5O_2C(CF_2)_4CO_2C_2H_5$	544.6	530.0	538.0	24.9
$C_3F_7CH_2O_2C(CH_2)_4CO_2CH_2C_3F_7$	752.2	750.6	728.7	24.0
$C_3F_7CO_2(CH_2)_5O_2CC_3F_7$	713.2	710.6	704.8	25.1
$C_3F_7CO_2(CH_2)_6O_2CC_3F_7$	752.2	750.6	753.8	25.8
$C_7F_{15}CO_2(CH_2)_5O_2CC_7F_{15}$	1162.8	1192.2	1114.0	24.1

The atomic parachor for fluorine (P_F), obtained from the experimental values using the Sugden constants (except for fluorine), range from 24.0 to 25.8. If the more recent constants given by Vogel[12] are employed, values from 22.2 to 24.0 are obtained. Schulman and Zisman[5] found similar variances in the few examples they studied. Fowler[4] reported values of 24.4–24.8 for P_F in fluorocarbons, which are lower than those assigned by Sugden[10] (25.7), Mumford and Phillips[11] (25.5) or Vogel[12] (26.1).

It is therefore difficult with the data now available to assign a definite value or a narrow range for the atomic parachor for fluorine, though what data have been accumulated seem to indicate that the earlier values may be somewhat high. It may, perhaps, be advisable to assign a parachor value to the CF_2 group instead of to a single fluorine atom. This system of assigning values to whole groups rather than to individual atoms has been suggested by Gibling.[13] It also takes into account the slight increase in parachor of the methylene group as the number of carbon atoms increases. This might also be applied to the CF_2 group. The bond parachors suggested by Vogel[14] may also prove useful. In this system a preliminary value of 28.2 has been assigned for the C–F bond. The present diesters give C–F bond parachors varying from 24.4 to 26.2.

Experimental

Measurements were made with a Du Noüy Interfacial Tensiometer (Precision direct reading model), using a platinum–iridium ring with a circumference of 6.015 cm. and $R/r = 53.8$.

Acknowledgment.—The author wishes to thank Mr. Ray Robinson for his assistance with the measurements.

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[8] H. W. Fox and C. H. Chrisman, Jr., *J. Phys. Chem.*, **56**, 284 (1952).

[9] This compound has not been described previously. Physical constants include: b.p. 52–53° (0.8 mm.), $n^{25}\mathrm{D}$ 1.3824 and $d^{25}{}_4$ 1.491.

[10] S. Sugden, "The Parachor and Valency," Routledge and Sons, Ltd., London, 1930.

[11] S. A. Mumford and J. W. C. Phillips, *J. Chem. Soc.*, 2112 (1929).

[12] A. I. Vogel, *J. Chem. Soc.*, 1842 (1948).

[13] J. W. Gibling, *ibid.*, 299 (1941); *ibid.*, 661 (1942); *ibid.*, 146 (1943).

[14] A. I. Vogel, W. T. Cresswell, G. J. Jeffery and J. Leicester, *Chemistry and Industry*, 358 (1950).

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The Compounds Formed between Nickel(II) and Dimethylglyoxime by Alkaline Oxidation

BY E. BOOTH AND J. D. H. STRICKLAND[1]

RECEIVED NOVEMBER 21, 1952

The determination of traces of nickel by dimethylglyoxime in the presence of alkaline oxidizing agents is established analytical practice. Difficulties still encountered, in particular the formation[2a] of a "metastable" complex, are largely explained by the discovery by Hooreman[2b] of two complexes with markedly different absorption spectra, and containing nickel and dimethylglyoxime (DMGOH) in the ratio 1:2 and 1:4. (For brevity we shall refer to them as complexes I and II, respectively.)

Isolation in the solid state of these complexes is very difficult and we believe that the substances isolated and analyzed by authors such as Feigl,[3] Kuras and Ruzicka[4] or Okac and Polster[5] are not the same as those present in solution during analytical methods for traces of nickel. Whilst disagreeing with the findings of Babko,[6] we do agree that techniques such as spectrophotometry are the most reliable for elucidating the formulas of compounds of this type and we have used such methods exclusively.

Experimental

Absorption Spectra.—The absorption spectra of complex I and complex II, were obtained at 3.75×10^{-5} *M* concentrations.

Complex I had two peaks in the visible, the molar extinction coefficients being 1.16×10^4 (442 mμ) and 0.52×10^4 (530 mμ). The oscillator strength, *f*, of the main peak was approximately 0.16 per nickel atom. The single broad peak of complex II had a molar extinction coefficient of 1.28 ×

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[1] The British Columbia Research Council, Vancouver 8, Canada.

[2] (a) N. H. Furman and B. McDuffie, Atomic Energy Commission Classified Report AEC-M-4234 (1947); (b) M. Hooreman, *Anal. Chim. Acta*, **3**, 635 (1949).

[3] F. Feigl, *Ber.*, **57**, 758 (1924).

[4] M. Kuras and E. Ruzicka, *Chem. Listy*, **45**, 100 (1951).

[5] A. Okac and M. Polster, *Collection Czechoslov. Chem. Communs.*, **13**, 561 (1948).

[6] A. K. Babko, *Zhur. Anal. Khim.*, **3**, 284 (1948).

10^4 (460 mμ) with an oscillator strength of approximately 0.32 per nickel atom.

The Ratio of Combined Nickel and Dimethylglyoxime.—Having established conditions under which either one of the pure complexes could be formed, the ratio of reactants was established by a simplification of the method of variations. Plots of moles of DMGOH against the extinction of complex formed per mole of nickel reacting showed breaks at Ni: DMGOH ratios of 1:2 and 1:4, confirming the findings of Hooreman.[2]

Oxidation State of the Complex.—The amount of oxidant required to form a known amount of complex is made difficult to determine by the variety of side reactions which can take place. The concentrations of reactants must be less than about 10^{-3} *M* and the alkali stronger than 0.05 *M*; otherwise the red divalent complex is precipitated before oxidation is complete. The only way of ensuring no complications is to have stoichiometric quantities of nickel and DMGOH initially present and to find conditions such that these react to give a complete yield of complex.

Figure 1 shows experiments with complex II under these conditions, it will be seen that three electrons per nickel atom are involved in the formation of this substance.

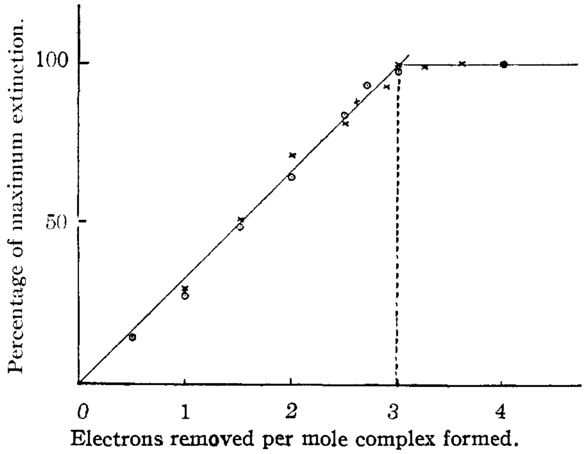

Fig. 1.—Oxidation state of complex II: x-x-x, 2.5 × 10^{-4} *M* complex formed; -·-·, 5 × 10^{-5} *M* complex formed.

Comparable experiments with complex I were only semiquantitative due to the possibility of oxidation of the ammonia, which is necessary for the formation of this complex. However, if two moles of DMGOH is added to a solution of one mole of complex I a rapid transformation of this compound into complex II occurs, the speed or completion of this reaction being unaltered by the presence or absence of dissolved air or hypohalite (the oxidant used for the formation of the complexes). It occurs equally readily even in the presence of excess of arsenite. These facts, and the general similarity of the two compounds, indicate that they are both in the same, $-3e^-$, oxidation state. Furthermore if the black unstable compound of trivalent nickel described by Edelman[7] is shaken with aqueous alkali, complexes I or II are formed according to whether the alkali is ammonia or sodium hydroxide.

x = No. of moles of DMGOH; ϕ = *p*H to which all titrations are taken; w = equivalents of OH^- to give ϕ without DMGOH present; w_1 = equivalents of OH^- to give ϕ with DMGOH present; y = back titer, in equivalents; y_1 = blank back titer, in equivalents; p = yield of complex.

$x \times 10^4$	ϕ	$w \times 10^4$	$w_1 \times 10^4$	$(w_1 - w) \times 10^4$	$y \times 10^4$	$y_1 \times 10^4$	$(y_1 - y) \times 10^4$	p	No. of OH^- ions used
6.90	10.46	1.46	4.26	2.80	295.2	302.4	7.2	1.00	5.9
6.90	10.46	1.46	4.26	2.80	294.2	302.3	8.1	1.00	6.4
13.80	10.68	2.36	10.06	7.70	268.4	280.5	12.1	0.93	6.3
13.80	10.68	2.36	10.06	7.70	268.4	280.5	12.1	0.93	6.3

The Nature of the Complexes in Solution.—Complex II is anionic. It is not extracted by organic solvents and migrates to the anode in electromigration experiments. It enters the resin phase when shaken with an anion exchanger, *e.g.*, Amberlite 400, and using this resin and the technique recently outlined[8] the ion was shown to be monovalent.

Complex I, however, would not enter the resin phase of either an anion or a cation exchanger. It remained inert during electromigration experiments and could be extracted into *n*-butyl alcohol. The molecule must be assumed to be neutral.

Both compounds are destroyed by acidifying solutions but in alkali (*p*H > 10.5) complex II is stable indefinitely. Complex I, however, decomposes appreciably over a period of hours. According to conditions it will either decompose completely, form the red Ni(II) complex or change partially to complex II. The latter, although formed easily from complex I by adding DMGOH, cannot, once formed, be converted back to complex I by any means we have been able to devise.

The Number of Hydroxyl Ions Required.—Acidity changes occurring during the formation of complex I and II are difficult to measure by *p*H experiments as the concentrations of the reacting species are necessarily small in comparison with the concentration of alkali which must be present for the reaction to take place satisfactorily. With complex I, where ammonia must be present, the further complication of buffering makes such experiments almost impossible but the number of OH^- groups used up in the reaction to form complex II has been measured as follows.

One hundred fifty ml. of 0.2 *N* sodium hydroxide was neutralized by 0.2 *N* acid to *p*H 7. Fifty ml. of water was added and 0.1 *N* sodium hydroxide (w equivalents) to bring the *p*H to ϕ (about 10.5). This experiment was repeated but adding x moles of DMGOH as pure solid and a larger, w_1, number of equivalents of 0.1 *N* akali to make the *p*H ϕ $w_1 - w$ equivalents were thus used to ionize the DMGOH to $DMGO^-$.[9]

In the main experiments x moles of DMGOH was added to 150 ml. of 0.2 *N* alkali followed by w_1 equivalents of alkali, and water to give a volume of exactly 200 ml. Twenty ml. of a solution of nickel nitrate (0.25 x equivalent Ni^{II}) in bromine water (1.5–1.75 times the theoretical oxidant) was introduced dropwise at a temperature of 35°. The solution was then cooled to 25° and 5 ml. withdrawn to determine the fractional yield, p, of complex II formation. The solution was slowly titrated to *p*Hϕ with 0.2 *N* acid, and the number of equivalents, y, determined. A blank experiment was carried out exactly as above but adding no DMGOH and only w equivalents of excess alkali. Small additions of bromine, $nickel^{II}$ and DMGOH were made to the blank, these being equivalent to any such amounts left unreacted in the main experiment. Five ml. of solution was removed and discarded. If y_1 equivalents were then needed in the back titration of the blank then the number of equivalents of OH^- used up per mole of complex II formed is given by

$$\frac{4[(y_1 - y) + (w_1 - w)]}{\text{p.x.}} \times 220/215$$

the factor 220/215 being a volume correction.

The difference $y_1 - y$ on which the accuracy of this work depended was of the order of 5 ml. the over-all accuracy being better than ±0.5 of a mole of OH^-. Results of four such experiments are shown in the table. The mean value approximates to 6.

Combined Ammonia in Complex I.—Although complex II may be prepared in alkali hydroxide as well as ammoniacal solutions, and thus cannot contain combined ammonia molecules, all evidence points to the presence of the latter, in

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[7] L. E. Edelman, This Journal, 72, 5765 (1950).

[8] J. D. H. Strickland, *Nature*, **169**, 620 (1952); *ibid.*, **169**, 738 (1952).

[9] A. K. Babko and P. B. Mikhelson, *Zhur. Anal. Khim.*, **6**, 267 (1951).

some form, in complex I. Thus complex I cannot be formed, whatever the nickel:DMGOH ratio, unless ammonia is present in solutions. When solutions of complex I are stripped of ammonia by diffusion, etc., the complex decomposes before the ammonia is completely removed. When primary amines, *e.g.*, monoethylamine, are used instead of ammonia a compound similar to complex I is produced having an absorption spectrum almost identical with complex I except that the peak at 530 mμ found with complex I, is altered in shape and size and it is to be inferred that this absorption arises from an ammonia group in the molecule. It is also significant that only ammonia will give complex I from Edelman's black solid.[7]

Discussion

The experimental data given above are mutually consistent and lead to the equation of formation of complex II to be given as

$$Ni^{2+} + 4DMGOH + 6OH^- \longrightarrow [Ni(OH)_2(DMGO)_4]^{1-} + 4H_2O + 3e^-$$

with the compound having the empirical formula shown. However its structure remains to be determined. The valency of the nickel is also uncertain, although it seems likely that one electron is removed in raising Ni^{II} to Ni^{III} and the other two are removed from the two hydroxyl groups. The very high molecular extinction coefficient of this compound would indicate resonance.

It would be logical to assume complex I to be an analogous compound with amino groups replacing two of the four dimethylglyoxime groups, but in the absence of evidence of the number of ammonia molecules involved this cannot be verified.

Complex I is formed almost exclusively in all published analytical methods but it would be much better to use complex II, as the former is unstable and can either decompose or partially revert to complex II in a comparatively short time. To achieve rapid and quantitative formation of complex II a good initial excess of dimethylglyoxime should always be present with only the minimum amount of oxidant (2–3 ml. of 0.01 *N* iodine or bromine), so that excess dimethylglyoxime is not oxidized before it can convert any complex I to II. The ammonia present in solutions should be kept to a minimum and the correct alkalinity (*p*H > 11) obtained by adding sodium hydroxide.

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Condensations of Primary Aliphatic Nitramines with Formaldehyde

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In the course of some studies of the chemistry of primary aliphatic nitramines we have observed a convenient condensation of formaldehyde with several primary nitramines in strong sulfuric acid leading to the formation of N,N′-dialkylmethylenedinitramines.

$$2RNHNO_2 + CH_2O \xrightarrow{ca.\ 90\%\ H_2SO_4} \underset{(I\text{–}IV)}{[RN(NO_2)]_2CH_2} + H_2O$$

I, $R = CH_3$
II, $R = C_2H_5$
III, $R = n\text{-}C_4H_9$
IV, $R = \text{–}CH_2\text{–}$

Thus formaldehyde seems to stabilize the primary nitramines to strong sulfuric acid. Holstead and Lamberton[1] have recently noted a quite analogous reaction (equation A) in which intermediately formed formaldehyde and nitramide (NH_2NO_2) condense with acetanilide under similar conditions.

$$AcO[CH_2N(NO_2)]_3CH_2OAc \xrightarrow[\text{concd. } H_2SO_4]{C_6H_5NHAc} (p\text{-}AcNHC_6H_4CH_2)_2NNO_2 \quad (A)$$

The yields from the condensation reaction are only fair, probably due to the concurrent decomposition of the nitramines in the strong acid.[2] Since low temperatures (below 0°) and very efficient stirring were found to be necessary for good results, *ca.* 90% sulfuric acid solutions were used to permit these conditions. A complete study of the reaction variables was not made and the listed yields are probably not optimum. Compound IV was more conveniently prepared by the cyclization of the monomethylol derivative of ethylenedinitramine[3] in the strong sulfuric acid solution. The methylol derivatives of primary aliphatic mononitramines are unknown, probably due to an unfavorable equilibrium.[4]

Cyclohexyl nitramine failed to react similarly to the other primary nitramines and it was not found possible to identify any products from the reaction. Nitrourethan also failed to condense with formaldehyde under the chosen experimental conditions and could be recovered from the acid solution. The very low basicity of the compound probably prevents the condensation. Attempts to employ chloral or paraldehyde in place of formaldehyde were unsuccessful.

The use of the Lewis acid, boron trifluoride, as a substitute for the sulfuric acid is briefly noted in the experimental section.

Compounds III and IV showed the typical secondary nitramine ultraviolet spectrum[5] having λ_{max} 240 mμ(ε 11,300) and λ_{max} 235 mμ (ε 11,500), respectively, when measured in absolute ethanol.

Compounds (I–IV) appear to be useful intermediates in the synthesis of some substituted hydrazines and experiments, with this object in mind, are in progress.

Experimental[6]

The primary mononitramines were prepared by nitration of the appropriate N-alkyl urethans,[7] ammonolysis, in dry

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[1] C. H. Holstead and A. H. Lamberton, *J. Chem. Soc.*, 1886 (1952).

[2] (a) A. P. N. Franchimont and E. A. Klobbie, *Rec. trav. chim.*, **7**, 12 and 236 (1888); (b) M. H. van Erp. *ibid.*, **14**, 1 (1895); (c) A. P. N. Franchimont and H. Umbgrove, *ibid.*, **17**, 287 (1898); (d) A. P. N. Franchimont, *ibid.*, **29**, 296 (1910); (e) J. Thiele and A. Lachmann, *Ann.*, **288**, 267 (1896); (f) A. H. Lamberton, *Quart. Rev.* (*London*), **5**, 75 (1951).

[3] (a) D. Woodcock, *J. Chem. Soc.*, 1635 (1949); (b) W. E. Bachmann, W. J. Horton, E. L. Jenner, N. W. MacNaughton and C. E. Maxwell, III, THIS JOURNAL, **72**, 3132 (1950).

[4] A. H. Lamberton, C. Lindley, P. G. Owston and J. C. Speakman, *J. Chem. Soc.*, 1641 (1949).

[5] R. N. Jones and G. D. Thorn, *Can. J. Research*, **27B**, 828 (1949).

[6] Melting and boiling points are not corrected.

[7] H. M. Curry and J. P. Mason, THIS JOURNAL, **73**, 5043 (1951)