TABLE II

Salt	M.p., °C.
$(CH_3)_3N(C_2H_5)I$	300 (dec.)
$(C_2H_5)_4NI$	283.8–284.0
$(n\text{-}C_3H_7)_3N(C_2H_5)I$	240.0–240.4
$(n\text{-}C_4H_9)_3N(C_2H_5)I$	202–203
$(C_6H_5)N(CH_3)_2(C_2H_5)I$	135–136
$(C_6H_5)N(C_2H_5)_3I$	124–125
$(NCCH_2)N(C_2H_5)_3I$	182–183 (dec.)
$(NCCH_2CH_2)N(C_2H_5)_3I$	167–189 (dec.)

c.p.s. using an Industrial Instruments, Inc., Model RC 16 B 1 conductivity bridge.

Standard solutions of hydroiodides were made up by adding 30% hydriodic acid to an excess of the amine in acetone. The concentration of iodide was determined by Volhard titration. The effect of the water added on the conductivity of the solution was checked by measuring the conductivity of pure tributylamine hydroiodide with and without added water. Within the concentration ranges used in this investigation, no change in conductivity was noted.

Conductometric kinetic runs of tertiary and secondary amines were made as described previously.[2] Solutions 0.1 *N* or less in amine and ethyl iodide were made up in 50-ml. volumetric flasks. The two solutions were placed in a thermostatted water bath maintained within the limits 35.00 ± 0.01°. After a minimum of 30 min., 40-ml. aliquots of each solution were withdrawn with thermostatted pipets and mixed by shaking in a 100-ml. thermostatted volumetric flask. The solution was then transferred to the conductivity cell immersed in the bath. At appropriate intervals, the time and resistance were recorded.

In the case of primary amines, the amine was added directly to a thermostatted solution of ethyl iodide in acetone, and the kinetic run was made immediately after mixing in the same manner as above.

Titrimetric kinetic runs were run on solutions made up as above, and kept in the thermostatted volumetric flask sealed with a rubber stopple. At appropriate intervals, approximately 4-ml. samples of the reaction mixture were removed from the flask using a syringe and long hypodermic needle. An exact 3-ml. aliquot of the removed sample was immediately quenched in 10 ml. of acetone and 10 ml. of water. The time was measured from the beginning of shaking to the instant of quenching. The aqueous acetone solution was extracted three times with 10-ml. portions of ether and then titrated by the Volhard method, as were the standard ammonium salts.

The Ultraviolet Absorption Spectra of Methazonic Acid and Its Sodium Salts

D. J. MORGAN[1]

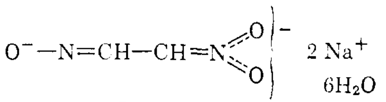
Research Department, British Nylon Spinners Ltd., Pontypool, Mon., England

Received June 19, 1962

The ultraviolet absorption spectra of methazonic acid and its sodium salts have been studied in aqueous solution at various pH values.

In agreement with published values,[2a,b] the spectrum of disodium methazonate in water (Fig. 1a) has a band at 298 mμ (ϵ_{max} 17,800) which deviates slightly from Beer's law at higher concentrations (Fig. 3a). There is, however, a second, less intense, band at 220 mμ (ϵ_{max} 5400) which obeys Beer's law up to a concentration of at least 0.005% (Fig. 3b).

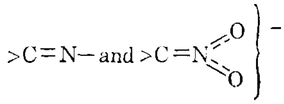
Both bands are unchanged after the solution has been left for two weeks. The structure of disodium methazonate is thought[3] to be I so that the



$$\left[O^-{-}N{=}CH{-}CH{=}N\overset{O}{\underset{O}{\lessdot}}\right]^- \; 2\,Na^+ \; 6H_2O$$

I

more intense band can therefore be ascribed to a π→π transition in the conjugated structures



$$>C{=}N{-} \text{ and } \left[>C{=}N\overset{O}{\underset{O}{\lessdot}}\right]^-$$

In 0.01 *N* sodium hydroxide, this band is displaced to longer wave lengths (Fig. 1b) and is intensified (λ_{max} 310 mμ; ϵ_{max} 18,500) suggesting that complete formation of the resonating nitroxylate ion is not attained until a pH value of about 12 units. This observation confirms that of Matthew and Kubler,[2b] who give a value for the specific extinction coefficient of methazonic acid in *N* potassium hydroxide at 310 mμ of 197.3, which corresponds to a molar extinction coefficient[4] of 20,520. These values can be compared with that of dimethyl glyoxime in 0.1 *N* sodium hydroxide (λ_{max} 270 mμ; ϵ_{max} 17,700), where the band is ascribed to a π→π transition in the two conjugated —C=N—O⁻ structures; replacement of the —N—O⁻ ion by the nitroxylate ion, which is itself a resonating structure, would account for the

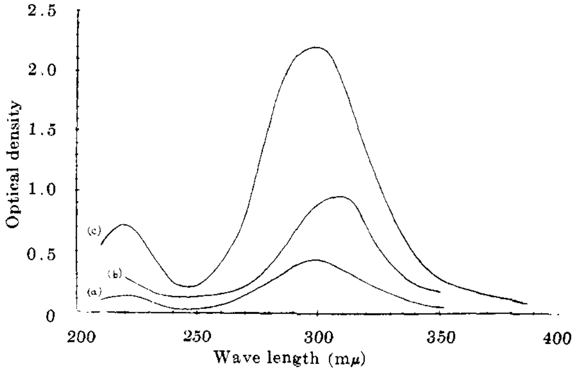


Fig. 1.—Ultraviolet absorption spectra: (a) disodium methazonate in water, 0.025 mmoles/l.; (b) disodium methazonate, in *N*/100 sodium hydroxide, 0.05 mmole/l.; (c) monosodium methazonate in water, 0.016 mmole/l.

---

[1] Present address: United Kingdom Atomic Energy Authority, Health Physics and Medical Division, Atomic Energy Research Establishment, Harwell, Nr. Didcot, Berks., England.

[2] (a) C. M. Drew, J. R. McNesby, and A. S. Gordon, *J. Am. Chem. Soc.*, **77**, 2622 (1955); (b) V. E. Matthews and D. G. Kubler, *J. Org. Chem.*, **25**, 266 (1960).

[3] D. J. Morgan, *ibid.*, **23**, 1069 (1958).

intensification and shift to longer wave length which is observed in the spectrum of disodium methazonate in alkaline solution.

In 0.0020% aqueous solution, the spectrum of monosodium methazonate (Fig. 1c) is identical in shape with that of disodium methazonate, and contains two high intensity bands characterised by λ_{max} 220 mμ; ϵ_{max} 4670 and λ_{max} 298 mμ; ϵ_{max} 14,000, the pH value of the solution being 6.5 units. Moreover, when a 0.0026% aqueous solution of disodium methazonate (which is approximately equivalent to a 0.0013% solution of monosodium methazonate) is acidified to this pH, the extinction coefficient at 298 mμ is 16,000, indicating once again that Beer's law is not obeyed at this pH value.

Matthews and Kubler,[2b] from their observations on the spectrum of methazonic acid in alkaline solution, suggest that the peak in the absorption spectrum at 298 mμ is due to the mono (potassium) salt and gave a value for the specific extinction coefficient of 115.3, which corresponds to a molar extinction coefficient[4] of 12,000 (their value 16,407).

Our observations, however, do not confirm their suggestion as the peak at 298 mμ is definitely present in the spectrum of both mono- and disodium methazonate.

Since the spectrum of monosodium methazonate is identical in shape with that of disodium methazonate but is slightly less intense, it can therefore be ascribed to a similar transition in the same conjugated system as occurs in the latter.

In the spectrum of methazonic acid in aqueous solution, there is one high intensity band with an absorption maximum at 298 mμ (Fig. 2a) which deviates markedly from Beer's law (Fig. 3c) and which has a maximum molar extinction coefficient of 13,400 at a concentration of 0.0001%. As with monosodium methazonate, this maximum occurs at the same wave length as, but is considerably less intense than, the stronger band observed in the spectrum of disodium methazonate. This suggests that the structure of the acid in 0.0001% aqueous solution is basically the same as that of the disodium salt and is most likely represented by II

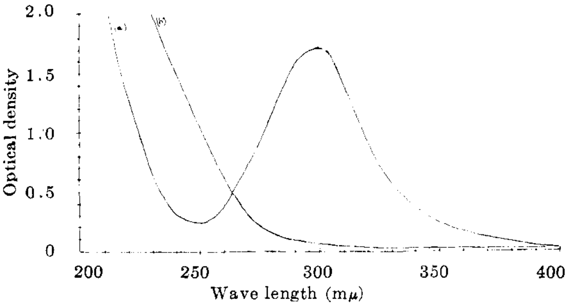


Fig. 2.—Ultraviolet absorption spectra of methazonic acid, 0.43 mmole/l.: (a) immediately after dissolution, (b) after standing for one week.

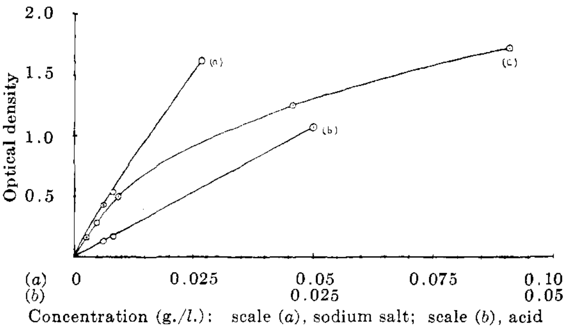
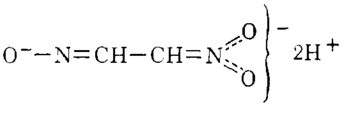


Fig. 3.—Variation of optical density with concentration: (a) disodium methazonate, λ = 298 mμ; (b) disodium methazonate, λ = 220 mμ; (c) methazonic acid, λ = 298 mμ.



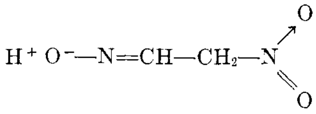
$$\left\{O^{-}-N{=}CH-CH{=}N\overset{O}{\underset{O}{\lessgtr}}\right\}^{-} 2H^{+}$$

II

This is a fully conjugated structure which would therefore be expected to be stable, as is shown by the fact that the spectrum of the 0.001% solution is unchanged on standing for a week.

The spectrum of a more concentrated (0.043%) solution changes completely on standing, however, the absorption maximum at 298 mμ vanishing completely (Fig. 2b).

Solid methazonic acid is very unstable and normally decomposes fairly rapidly on standing. Its infrared spectrum contains a very strong band at 1573 cm.$^{-1}$ which can be assigned to the NO_2 asymmetric stretch and it is suggested that the structure of the solid is probably III.



$$H^{+}\,O^{-}-N{=}CH-CH_2-N\overset{\nearrow O}{\underset{\searrow O}{}}$$

III

The instability of methazonic acid in the solid state is comparable with that of the 1,2-dinitroparaffins which it closely resembles in structure. In contrast, the complete stability of its structural isomer, ethylnitrolic acid, is ascribed to very strong hydrogen bonding[5] which is very unlikely in the case of methazonic acid, as it would involve formation of a seven-membered ring.

Since it is known that the rate of tautomerism of *aci*-nitro compounds in solution to the true nitro

---

[4] Matthews and Kubler state that the specific extinction coefficient k of 197.3 corresponds to a molar extinction coefficient of 28,086. This appears to be an error, however, for if a compound of molecular weight M_1 and concentration C_1 is converted to one of molecular weight M_2, *e.g.*, by dissolving an acid in aqueous alkaline solution, then the concentration of the second compound $C_2 = M_2/M_1$ and, therefore, the molar extinction coefficient of the second ϵ_2 will be given by $\epsilon_2 =$

$$\frac{k_2 \times M_2}{(M_2/M_1)C_1} = \frac{k_2 M_1}{C_1}$$

i.e., ϵ_2 is still expressed in terms of the molecular weight of the original compound, M_1, and not in terms of the molecular weight of the product, M_2. In this case, then, $\epsilon_2 = 197.3 \times 104 = 20{,}520$.

[5] D. J. Morgan, *J. Appl. Chem.*, **9**, 201 (1959).

structure is proportional to the concentration of the nitroxylate or *aci*-ions,[6] the instability of the concentrated solutions, as evidenced by the change in the spectra in standing, is to be expected, as it would correspond to the formation and decomposition of the unstable true nitro compound.

The Effect of Mineral Acid on the Spectra (Fig. 4). On acidification of a 0.0026% aqueous solution of disodium methazonate hexahydrate with dilute hydrochloric acid, no change in the molar extinction coefficient at 298 mμ occurs until a pH of about 6 is reached (Fig. 4). This is what would be expected from the observed neutralization curve of the salt (Fig. 5), from which we see that

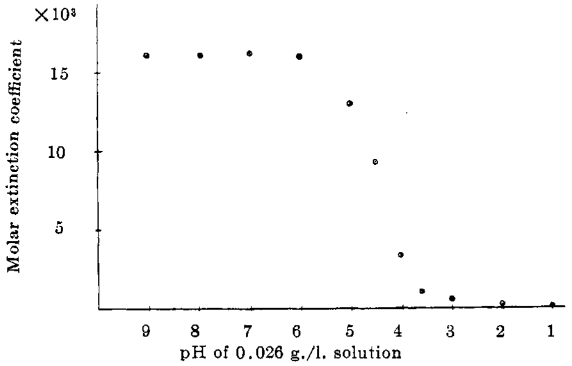


Fig. 4.—Variation of the molar extinction coefficient of the methazonate anion with pH of solution.

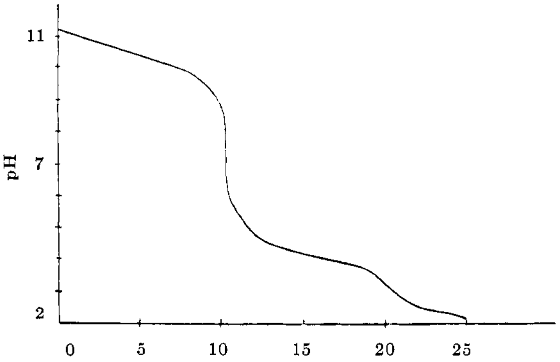
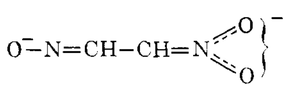


Fig. 5.—Variation of pH of a solution disodium methazonate with volume of acid added.

neutralization of the =N—O⁻ Na⁺ is more or less complete by a pH of 5 to 6 units. This would have no effect on the spectrum as the structure would still contain the conjugated system



$$O^{-}-N=CH-CH=N\left\{\begin{matrix}O\\O\end{matrix}\right\}^{-}$$

Below a pH of 5 however, the molar extinction coefficient falls rapidly, becoming 600 at a pH of 3, corresponding to the neutralization of the sodium nitroxylate. Further reduction of the pH has two effects: Ionization of the free nitronic acid formed is depressed by the mineral acid, whilst conversion of dissociated nitronic acid, *i.e.*, nitroxylate ions, to the true nitro form III occurs. The second effect would lead to a fall in extinction coefficient, as III contains a true nitro group and a >C=N— bond, separated by a methylene group, *i.e.*, unconjugated. When the pH is reduced to about 3, the band with a maximum at 298 mμ becomes much less pronounced in relation to the rest of the spectrum and by a pH of 2, has disappeared altogether.

In its place, a shoulder appears at 275 mμ (Fig. 6a) together with a feeble band at longer wave lengths (λ_{max} 355 mμ; ϵ_{max} 144), while in *N* hydrochloric acid (Fig. 6b), there are two distinct bands (λ_{max} 275 mμ; ϵ_{max} 69 and λ_{max} 355 mμ; ϵ_{max} 54). The band characterized by λ_{max} 275 mμ; ϵ_{max} 69 is indicative of an $n \rightarrow \pi$ transition such as occurs in the true nitro group.

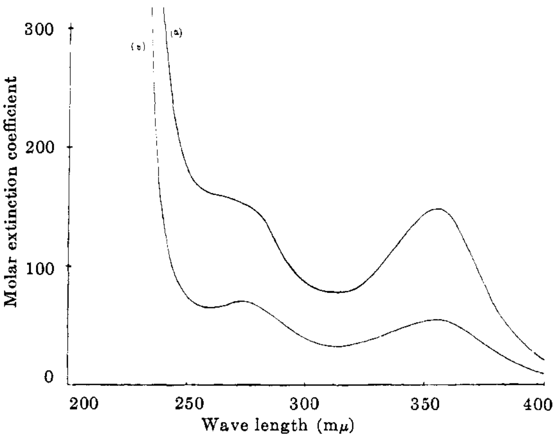


Fig. 6.—Effect of mineral acid on the spectrum of disodium methazonate.

It should however be noted that even a concentrated solution (1.04%) of disodium methazonate, which has been titrated with mineral acid to a pH of 2, units can be back-titrated along the same titration curve, provided that the back-titration is carried out immediately. This implies that formation of the true nitro compound is not instantaneous. If the solution in *N* hydrochloric acid is left to stand for five hours, however, and then brought to a pH of 12 with sodium hydroxide, then only a partial conversion to disodium methazonate occurs, the molar extinction coefficient at 310 mμ being reduced to 9500 instead of 18,500, showing that decomposition of some of the methazonic acid has occurred.

Sidgwick states[6] that it is the undissociated nitronic acid molecule which is unstable. Souchay and Armand[7] have examined the reaction between sodium *aci*-nitropane and mineral acid in detail. They found that conversion to the corresponding

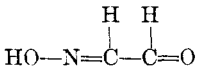
---

[6] N. V. Sidgwick, "The Organic Chemistry of Nitrogen," Clarendon Press, Oxford, 1945, p. 235.

[7] P. Souchay and J. Armand, *Compt. rend.*, **253**, 460 (1961).

ketone (*via* the intermediate formation of the undissociated nitronic acid) increased as the acidity of the solution was increased. We therefore suggest that the instability of methazonic acid in mineral acid solution is due to two causes.

First, there is the decomposition of the undissociated nitronic acid and second, there is the formation of the (unstable) true nitro compound, as evidenced by the low intensity band which appears at 275 mμ. By analogy with the work of Souchay and Arnold, the compound which would be formed from methazonic acid by the first mechanism would be the "semi-oxime" or isonitrosoaldehyde IV and although we were unable to isolate



$$\mathrm{HO{-}N{=}\overset{H}{\overset{|}{C}}{-}\overset{H}{\overset{|}{C}}{=}O}$$

IV

this from solution, we suggest that this compound, containing a carbonyl group conjugated with a $>C = N—$ bond could be responsible for the band characterized by λ_{max} 355 mμ; ϵ_{max} 54. Such a compound would be analogous to the α,β-unsaturated ketones, which have a low intensity band above 300 mμ. (This band is usually ascribed to the displaced band of the carbonyl group, *e.g.* mesityl oxide, λ_{max} 305 mμ; ϵ_{max} 95.) On making the acid solution alkaline once more, then the undecomposed true nitro compound would revert to mono- or disodium methazonate; this would be impossible with the "semi-oxime," which would account for the loss which we found.

A final point of interest which arose during the study of free methazonic acid was that although it is normally very unstable, decomposing to a red oil in a matter of days (*cf.* Matthews and Kubler), a few samples of the purified solid remained unchanged even after a weeks storage. This suggests that the instability of the majority of specimens may in fact be due to the presence of traces of free mineral acid.

Experimental

Disodium methazonate was prepared by the action of concentrated sodium hydroxide on nitromethane and the free acid and the monosodium salt isolated as described previously.[3] Spectral measurements were made on a Unicam SP500 spectrophotometer.

Synthesis of Polyfluorobenzenes

G. W. PARSHALL

Contribution No. 772 from the Central Research Department,
Experimental Station,
E. I. Du Pont de Nemours and Company,
Wilmington 98, Delaware

Received June 19, 1962

Hexafluorobenzene has been prepared by a variety of methods including pyrolysis of tribromofluoromethane,[1] dehydrofluorination of polyfluorocyclohexanes,[2] and fluorination of hexachlorobenzene.[3] In the present work hexafluorobenzene has been obtained by reaction of potassium fluoride with 1,2,4,5-tetrachloro-3,3,6,6-tetrafluorocyclohexadiene which is readily prepared from sulfur tetrafluoride and chloranil.[4]

The fluorination of the diene at 400–700° produces chloroperfluorobenzenes, perfluorocyclohexadiene, and chloroperfluorocyclohexadienes in proportions depending on the reaction conditions (Table I). High temperatures and long reaction times produce larger proportions of the aromatic products. Although the proportion of hexafluorobenzene was small even under the best conditions tried, substantial quantities of the chloroperfluorobenzenes were obtained. This reaction provides a superior synthesis of a new trichlorotrifluorobenzene, apparently the 1,2,4-isomer.

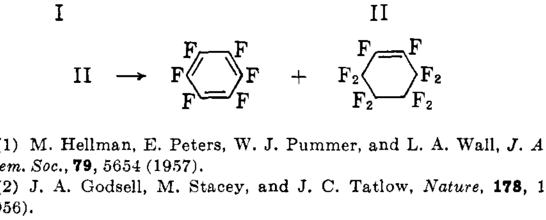
TABLE I

REACTION OF POTASSIUM FLUORIDE WITH TETRACHLOROTETRAFLUOROCYCLOHEXADIENE

	Reaction temperature			
	400°	525°	600°	700°
Weight of product as % of starting material	90%	65%	67%	21%
Product[a]				
Hexafluorobenzene	Trace	5	8	17
Chloropentafluorobenzene	1	12	16	24
Dichlorotetrafluorobenzene	7	28	14	21
Trichlorotrifluorobenzene	6	17	7	5
Octafluoro-1,4-cyclohexadiene	...	2	1	3
Chloroheptafluorocyclohexadiene	...	9	7	11
Dichlorohexafluorocyclohexadiene	1	9	12	9
Trichloropentafluorocyclohexadiene	10	Trace	1	..
Tetrachlorotetrafluorocyclohexadiene (starting material)	75	4	2	..
Decafluorocyclohexene	...	1.3	1.3	2.7

[a] The yields are expressed in area per cent from gas chromatographic analysis of the crude reaction product.

The fluorination and aromatization of the diene (I) appear to occur in discrete, successive steps. Chlorine atoms are displaced in a stepwise manner to give ultimately, perfluorocyclohexadiene (II).



---

[1] M. Hellman, E. Peters, W. J. Pummer, and L. A. Wall, *J. Am. Chem. Soc.*, **79**, 5654 (1957).

[2] J. A. Godsell, M. Stacey, and J. C. Tatlow, *Nature*, **178**, 199 (1956).

[3] W. B. Liggett, V. V. Lindgren, and E. T. McBee, U.S. Patent 2,461,554 (1949).

[4] W. R. Hasek, W. C. Smith, and V. A. Engelhardt, *J. Am. Chem. Soc.*, **82**, 543 (1960).

[5] W. T. Miller, W. Frass, and P. R. Resnicke, *ibid*, **83**, 1767 (1961).