Tautomeric Forms of Oxy- and Oxo-derivatives of 1,3,5-Triazine. Part VI. Isomerization Mechanism and Thermal Stability of the Methyl Esters of Cyanuric Acid.

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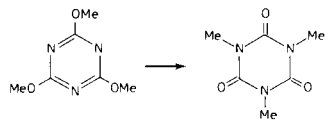
Previous investigations of the kinetics and the mechanism of the thermal isomerization $C_3N_3(OMe)_3 \rightarrow C_3(NMe)_3O_3$ have been continued with a study of the isomerization mechanism of the mixed *O,O,N*- and *O,N,N*-trimethyl esters of cyanuric acid. A full discussion of the overall process is given, in which it is assumed that the above mixed esters are intermediates.

It is shown that the tautomeric transformation occurs as the consequence of the attack of Me^+ cations on the ring nitrogen of the neutral molecules. The presence of such cations in the melt was established by ionic exchange with the H^+ of the molten acids. It is also shown that the tautomeric transformation in solution proceeds with the same mechanism.

An explanation is proposed for the thermal instability of the mixed esters (which isomerize even in the solid state, more than 20° below their melting point), which is based on the high polarity of these molecules. This property is discussed in terms of electronic structure calculations carried out with the Pariser-Parr-Pople approximation of the A.S.M.O., S.C.F., method.

A previous paper of this series (1) reported studies on the kinetics of the thermal isomerization of trimethoxy-*s*-triazine, I, to its tautomeric form, II, the *N,N,N*-trimethyl ester of cyanuric acid. This reaction was carried out on the substance, when melted in a sealed tube, at three different temperatures, 212, 225 and 238°, and the residual mole fraction x present at a given time was determined from the area of its infrared absorption band at 7.35 μ.



I II

The plot of x^{-1} versus time was linear up to 2/3 transformation, and the rate constants, obtained from a least square treatment of the data, were as follows:

$10^3 \cdot k$, sec^{-1}	°C
0.47 ± 0.01	212
1.024 ± 0.018	225
2.104 ± 0.039	238

The Arrhenius plot of these constants gave an apparent activation energy of 28.3 ± 0.8 kcal/mole. These results, although making an intramolecular rearrangement very unlikely, gave no hint as to a possible mechanism.

A more detailed analysis of the process was subsequently carried out (2) by separately labelling the migrating methyl groups with deuterium and the substituted triazine ring with oxygen-18, and by using suitable mixtures of three different isotopic molecules: $C_3N_3(O^{16}CH_3)_3$, mass 171; $C_3N_3(O^{18}CH_3)_3$, mass 177; $C_3N_3(O^{16}CD_3)_3$, mass 180. The mass spectroscopic measurement of the peak intensity of the molecular ions gave the changes in the isotopic composition of each mixture caused by the reaction. Starting with a mixture of isotopic molecules of mass 177 and 180 in the mole ratio 1:1, all the possible masses 171, 174, 177, 180, 183 and 186 were found in the reaction product. The formation of the isotopic species 171 implied the migration of three methyl-*H* groups from the O^{18}- to the O^{16}-cyanuric acid ring, and the species 186 implied the migration of three methyl-*D* groups from the O^{16}- to the O^{18}-labelled ring.

The data obtained from several 1:2, 1:1 and 2:1 reaction mixtures of different isotopic starting species, which had been transformed under various conditions, were

analyzed assuming that the CH_3 and CD_3 groups were statistically distributed among the available ring nitrogen positions. This model gave a complete and satisfactory agreement between the calculated and measured peak intensities, and also checked with previous kinetic measurements. Besides this evidence for a fully intermolecular process it was also possible to establish that:

(a) a limited exchange of methyl groups, about 2-3 mole percent of a given isotopic species, took place during the reaction between the methyl groups of I before its conversion to II;

(b) no exchange of the methyl groups occurred between the molecules of II up to 270°, the highest temperature at which the reaction was carried out;

(c) there was no evidence for a reverse reaction II → I and therefore the reaction was irreversible under the observed conditions;

(d) intermediate or decomposition products were not present in the reaction product.

In conclusion it was suggested (2) that methyl cations produced by the ionic dissociation of I were the active species of the process, but a discussion of the mechanism was postponed until further information could be obtained on the role of CH_3^+ in the process.

The purpose of this paper is to present a full discussion of a mechanism based on these ideas, to report a new evidence obtained to support it, and to interpret the results in terms of the electronic structure of the reacting molecules. This latter point will be shown to be essential for clarifying the role of substitutional symmetry in determining the thermal stability of the molecules and for a discussion of a supposed symmetry principle (3), according to which only symmetrically substituted derivatives of cyanuric acid should be formed.

THE REACTION MECHANISM

Although no evidence of intermediate steps was found in the reaction, their assumption seems to be unavoidable. As the reaction can only be an intermolecular one, a one-step process implies the simultaneous exchange of three methyl groups between two molecules colliding with their ring planes parallel, the *N*-atoms of one molecule facing the *C*-atoms of the other. A collision configuration of this type (corresponding to the arrangement of the molecules in the crystal lattice (4)) has already been shown (1) to agree with the kinetics, but it is contradicted by the results obtained with the *D*- and O^{18}-labelled molecules. The 1:1 reaction mixture referred to above should only contain molecules of mass 171 and 186, or at least a very large portion of them, and hardly any molecules of the intermediate masses, 174, 177, 180 and 183. The statistically equivalent distribution found for all isotopic molecular masses rules out such a possibility, and the only possible remaining mechanism are those where the Me groups migrate one at a time.

The mechanism now proposed starts with the ionic dissociation of I, and can be schematized as follows:

$$TT \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} A^- + Me^+ \qquad (1)$$

$$Me^+ + TT \xrightarrow{k_2} (TTMe)^+ \qquad (2)$$

$$(TTMe)^+ \xrightarrow{k_3} X_1 + Me^+ \qquad (3)$$

$$A^- + Me^+ \xrightarrow{k_4} X_1 \qquad (4)$$

$$X_1 \underset{k_{-5}}{\overset{k_5}{\rightleftarrows}} A_1^- + Me^+ \qquad (5)$$

$$Me^+ + X_1 \xrightarrow{k_6} (X_1Me)^+ \qquad (6)$$

$$(X_1Me)^+ \xrightarrow{k_7} X_2 + Me^+ \qquad (7)$$

$$A_1^- + Me^+ \xrightarrow{k_8} X_2 \qquad (8)$$

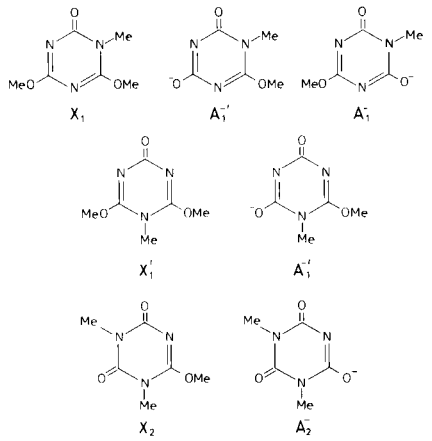
$$X_2 \underset{k_{-9}}{\overset{k_9}{\rightleftarrows}} A_2^- + Me^+ \qquad (9)$$

$$Me^+ + X_2 \xrightarrow{k_{10}} (X_2Me)^+ \qquad (10)$$

$$(X_2Me)^+ \xrightarrow{k_{11}} TTET + Me^+ \qquad (11)$$

$$A_2^- + Me^+ \xrightarrow{k_{12}} TTET \qquad (12)$$

Here TT stands for trimethoxytriazine (I), A^- for its anion, and TTET for the final product, trimethyltrioxohexahydrotriazine (II); X_i is the intermediate compound which has *i* methyl-substituted ring nitrogens, A_i^- is the anion originating from X_i by the detachment of one Me^+ of the methoxy group. It can easily be seen that there are two possible intermediates of type X_1 and two corresponding anions A_1^- but their explicit introduction into the reaction sequence would only make it longer. In fact, it is immaterial to this discussion of the mechanism as to which X_1 and A_1^- are formed or even if all of them are present.



(One of the anions from X_1 is the same as the anion from X_1', because they differ only in the formal localization of the negative charge.)

The first step in the process *(1)* justifies the Me group exchange in the starting material during the reaction. Steps *(2)*, *(6)* and *(10)* account for the statistical distribution of the Me groups and steps *(4)*, *(8)* and *(12)* represent a recombination of ions different from those considered in steps *(1)*, *(5)* and *(9)*. The rate of disappearance of TT during the process is defined as

$$-\frac{d[TT]}{dt} = k_1[TT] + k_2[Me^+][TT] - k_{-1}[A^-][Me^+]. \qquad (13)$$

The differential equations governing the rate of change of the other species can be written according to standard procedures. Using the electroneutrality condition

$$[A^-] + [A_1^-] + [A_2^-] = [Me^+] + [(TTMe)^+] + [(X_1Me)^+] + [(X_2Me)^+] \qquad (14)$$

the rate of change of the total anion concentration takes the form

$$\frac{d}{dt}\sum_{i=o}[A_i^-] = k_1[TT] + k_5[X_1] + k_9[X_2] - [Me^+]\sum_{i=o} g_i[A_i^-], \qquad (15)$$

where we identify A_0^- with A^-, and put

$$g_0 = k_{-1} + k_4,\quad g_1 = k_{-5} + k_8,\quad g_2 = k_{-9} + k_{12} \qquad (16)$$

Assuming that the total ionic species concentration is stationary, eq. *(15)* can be solved for $[Me^+]$ and eq. *(13)* can be written as:

$$-\frac{d[TT]}{dt} = k_1[TT] - k_{-1}[A^-][Me^+] + k_2[TT]\,\frac{k_1[TT] + k_5[X_1] + k_9[X_2]}{\Sigma\, g_i[A_i^-]} \qquad (17)$$

This is a fairly general equation for the mechanism and with some further assumptions, which help in getting a more detailed understanding of the process, it can be made to fit the observed kinetics. The simplest of these assumptions are: (i) the ionic dissociation of TT is very nearly at the equilibrium value during the reaction; (ii) the rate of conversion of both the X_1 and X_2 intermediates is so high that their concentrations under the reaction conditions are negligibly small. As a consequence,

$$k_1[TT] - k_{-1}[A^-][Me^+] = 0 \quad \text{or}$$

$$K = k_1/k_{-1} \qquad (18)$$

and

$$[X_1] \approx 0,\quad [X_2] \approx 0. \qquad (19)$$

Combining them with eq. *(17)* gives

$$-\frac{d\,TT}{dt} = k_1k_2[TT]^2/\Sigma\, g_i[A_i^-] \qquad (20)$$

which corresponds to the observed kinetics when the $\Sigma g_i[A_i^-]$ can be regarded as constant in time. This is strictly correct only when the assumed condition of stationary total ionic species concentration holds as the consequence of the individual anion concentrations remaining independent of time. This can be proven by considering, for example, the function of time $Q(t) = A(t) + \gamma_1 B(t) + \gamma_2 C(t)$, corresponding to eq. *(22)*. From eq. *(14)* and by equating eq. *(15)* to zero, it follows $A + B + C =$ const., and then $\dot{A} + \dot{B} = -\dot{C}$. Therefore $\dot{Q} = (1-\gamma_2)\dot{A} + (\gamma_1 - \gamma_2)\dot{B}$ and Q can be independent of time only when $\dot{A} = 0$, $\dot{B} = 0$, being given $\gamma_2 \neq 1$ and $\gamma_1 \neq \gamma_2$ as shown below in eq. *(22)*. However it is a fairly good approximation even with $\dot{A} \neq 0$ and $\dot{B} \neq 0$, until [TT] becomes so small that dilution effects start to play a significant role: then, according to eq. *(1)* and *(18)*, $[A^-]$ increases with time and the reaction is slowed down at a rate higher than the second order in [TT]. This change of rate was observed in our kinetic measurements at 238° above 2/3 transformation of TT (1).

The assumptions of eq. *(19)* imply first of all that steps *(5)* and *(9)* are far from equilibrium, and therefore $[A_1^-] \gg [X_1]$ and $[A_2^-] \gg [X_2]$. As a consequence the conversion of the X_i intermediates should occur mainly

through steps *(8)* and *(12)*. The ionic recombination of eq. *(4)* on the other hand is expected to be of minor importance in the production of X_1. These assumptions emphasize the determining role of certain steps and are equivalent to modifying eq. *(16)* as follows:

$$g_0 \approx k_{-1}, \quad g_1 \approx k_8, \quad g_2 \approx k_{12} \qquad (16)'$$

By substitution of these expressions in eq. *(20)* and using eq. *(18)*, the rate equation can be put into the simple form

$$-\frac{d[TT]}{dt} = \frac{K k_2}{Q} [TT]^2 \qquad (21)$$

where

$$Q = [A^-] + \gamma_1[A_1^-] + \gamma_2[A_2^-], \quad k_8 = \gamma_1 k_{-1},$$

$$k_{12} = \gamma_2 k_{-1} \qquad (22)$$

Within the limits where Q remains independent of time eq. *(21)* can be integrated with the condition $[TT]_0 = x_0 = 1$, at $t = 0$ (the reference state in the kinetic measurements (1) was 1 mole in 1 molar volume). This allows one to express the observed rate constant and the apparent activation energy as

$$k = K k_2/Q, \quad \Delta E^{\neq} = \Delta H^{\neq} + \Delta H_{diss} \qquad (23)$$

but the data available at this time does not enable one to determine K, k_2, $\Delta H^{\neq}$ or ΔH_{diss}.

TESTS OF THE PROPOSED MECHANISM

The mechanism proposed above fits the observed kinetics. This fitting however does not prove the mechanism itself so its implications will now be discussed and an attempt will be made to prove, as far as possible, the assumptions used above.

First of all, we neglected homolytic processes because of the absence of side-products or decomposition products: as previously reported (2), the mass spectra and the nuclear magnetic resonance spectra of the crude reaction material did not show the presence of anything besides TTET and eventually the unchanged starting TT. This can be regarded as evidence that only few, if any, recombinations of radicals have taken place.

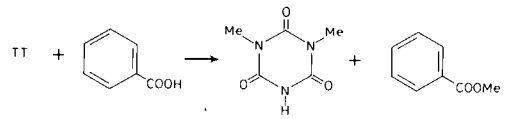
The following assumptions now need to be proved: (i) that methyl cations Me^+ are present in the molten TT; and (ii) that the attack of the Me^+ cations on the neutral TT molecules is the process which starts the isomerization reaction.

If Me^+ cations are present, as assumed, they should reveal themselves, *e.g.*, by undergoing exchange reactions with other cations of suitable ionic melts, such as the H^+ of the carboxylic acids. Moreover, if Me^+ reacts as assumed, a solution containing them should induce the transformation of dissolved TT into *N*-methyl derivatives, and possibly allow one to obtain the assumed X_1 and X_2 intermediates.

As will be seen below both reactions were found to occur as predicted and the assumed intermediates were obtained. Once these materials were available, it was also possible to prove the assumption that the intermediates had a conversion rate very much higher than that found with TT. Moreover, it will be proven that the last stage of the reaction mechanism, $X_2 \rightarrow$ TTET, is in agreement with the assumptions implied in the steps *(9)* to *(12)* of the scheme.

The H^+ - Me^+ Exchange Reaction.

Melting a 1:1 mole mixture of TT and benzoic acid together in a sealed tube, and keeping the melt at about 200°, leads (5) to the following reaction:

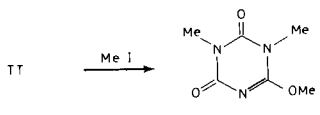


I III

This reaction goes to completion in less than one hour, and side-products were not detected. If the TT was slightly in excess of the 1:1 ratio a small amount of TTET was found to be present. The same reaction occurs under the same conditions when instead of TT one uses the *O,O,N*-trimethyl ester, X_1, or the other intermediate, the *O,N,N*-trimethyl ester, X_2, of cyanuric acid. Anisic acid, salicylic acid and phenylacetic acid can also be methylated by melting with TT or X_1 or X_2, and we propose that they be used as new methylating agents. The extension of the exchange reaction to H^+ donors of different types and to other cations is being investigated and will be reported later.

The Reaction with Me^+ in Solution.

The reaction with Me^+ in solution was first carried out using methyl iodide as the source of Me^+ and 1,4-dioxane as the solvent, and it was shown (6) that it gave the X_2 intermediate, without side-products:



I IV

When the solution, in a sealed tube, is heated at 100°, the reaction is completed in about 12 hours.

About fifty years ago Bilman and Bierrum (7) reported that TT reacts with methyl iodide (without solvent) to give TTET. They did not report having observed any intermediates. We have repeated their experiment and found that the product is always X_2, irrespective of whether methyl iodide is used as such or is diluted with about an equal volume of dioxane, acetone, ethyl acetate, benzene or iso-octane. The reason for this failure of Bilman and Bierrum to identify the *O,N,N*-trimethyl ester is probably related to the fact that its isomerization to TTET takes place in the solid, at a temperature well below the melting point, as will be shown in the next section.

In order to obtain evidence that this reaction with methyl iodide proceeds by the attack of Me^+ on the ring nitrogen atoms, as assumed in steps *(2), (3), (6)* and *(7)* of our mechanism, the fully deuterated compound TT-3(CD_3) (mass 180, over 99% isotopic purity (2)) was treated with methyl iodide at 100° in a sealed tube. The mole ratio methyl iodide:TT-3(CD_3) was 140:1 and the resulting isotopes were identified by their mass spectra as: (OCH_3, NCH_3, NCH_3)-171, 5.4%; (OCD_3, NCH_3, NCH_3)-174, 91.1%; (OCD_3, NCD_3, NCH_3)-177, 3.4%. This shows that over 94% of the product retained its CD_3 group on the oxygen atoms, while two methyl groups from the solvent became bound to the ring nitrogen atoms. There are however secondary reaction pathways in the solution, as shown by the presence of the (171)- and (177)-isotopes. The first one is certainly due to a limited exchange at the methoxy group. As will be seen below, this process occurs mainly with the reaction product. The (177)-isotope arises mainly from an intramolecular reaction, and only comes in a small measure from the CD_3 groups which have gone into the solvent. The upper limit for molecules formed by this latter process is about 1.3%, as can be easily calculated from the number of moles of the solvent CH_3, $2.37 \cdot 10^{-2}$, the starting TT, $1.75 \cdot 10^{-4}$ and assuming that the exchanged CD_3, $3.60 \cdot 10^{-4}$, is all available in the solvent. (A similar argument shows that the upper limit for the isotopes (OCH_3, NCD_3, NCH_3)-174 and (OCH_3, NCD_3, NCD_3)-177 is $< 0.2\%$.)

To rule out the possibility that the attachment of CH_3 to the ring nitrogen was due to replacement by an isotopic exchange of methyl groups after the reaction, the unlabelled *O,N,N*-trimethyl ester was heated in a sealed tube at 100° for 24 hours with deuteriomethyl iodide in the same mole ratio 140:1. The mass spectra showed that nearly 20% of the molecules had been converted to mass 174 but no molecules of mass 177 or 180 were present. In addition the peaks (m/e) = 56, 57, 58, corresponding to fragments containing an N-CH_3 group, had neither companion peaks of deuterated fragments nor other peaks up to 70. The CD_3 which entered into the molecules is therefore only bound to the oxygen atom and the exchange took place at the methoxy group. One thus concludes that the starting step of the reaction is the binding of the Me^+ present in the solution to the nitrogen of the dissolved molecules.

Another result which has been established is the stepwise nature of the reaction with methyl iodide. The reaction occurs very slowly at room temperature, and two weeks are necessary for about 50% conversion. The reaction mixture then contains, besides the starting material, the intermediates X_1 and X_2. Strong dilution with several solvents has also been found to slow down the reaction and to give a mixture of isomers. Methyl iodide diluted with ten times its volume of benzene, after 12 hours at 100°, gives 50% of the starting TT unchanged and about 25% of each of the two intermediates. When ethyl acetate is used as the solvent under the same conditions the reaction mixture contains 10% of X_1 and 45% of X_2. On the other hand, when the reaction is carried out with methyl iodide without solvent at 180°, the reaction gives only the end product TTET.

These reactions will not be further discussed here for the above examples give sufficient proof that the assumptions made about the role of Me^+ in the isomerization reaction are correct.

It is, however, convenient to mention at this point that a different synthesis of X_1 and X_2 was reported by Hantzsch and Bauer (8) in 1905. They proved the structure of these compounds by acid hydrolysis, which gave the *N*-methyl- and the *N,N*-dimethylcyanuric acid as products. We repeated their hydrolysis reaction, found that they proceeded as described (8) and therefore believe that Hantzsch and Bauer actually obtained these products. The fact that Slotta and Tschesche (9) were not able to duplicate the work described by Hantzsch and Bauer was probably due to the low thermal stability of these substances, which will be discussed below. This same circumstance also misled Slotta and Tschesche in several other ways because after repeating the methylation of *O,O*-dimethylcyanuric acid with diazomethane, just as they have described (9), we found that it produced about 35% of the desired *O,O,N*-trimethyl ester (10).

The Thermal Isomerization of the Intermediates.

The synthesis and isolation of X_1 and X_2 made it possible to test the proposed mechanism at two further points: the rate, and the mechanism of their conversion.

When the first intermediate, *O,O,N*-trimethyl ester was heated at its melting point, 148°, for 10 minutes it was converted into a mixture which contained about 10% of the starting product, 10% of the second intermediate and 80% of TTET. The conversion was practically complete after 30 minutes when only TTET was found to be present.

The conversion of the second intermediate, the *O,N,N*-

trimethyl ester was much faster, being complete after 20 minutes at 135° or after 8 minutes at 160°.

The conversion of both intermediates started, however, in the solid phase, well below their respective melting points. The observed melting temperature depends on the rate of heating, and this might explain why the melting point, reported by Hantzsch and Bauer (8), for X_1 was 105°.

The complexity of the mixture formed during the thermal isomerization of X_1, and the fact that a significant part of the reaction takes place, in both cases, in the solid phase during the 10-20 seconds required for melting, has so far prevented us from carrying out accurate measurements of the conversion rate constants when the bath is only a few degrees above the melting point. Some preliminary data on the conversion rate of the solid X_2, plotted in Fig. 1 and summarized in the experimental

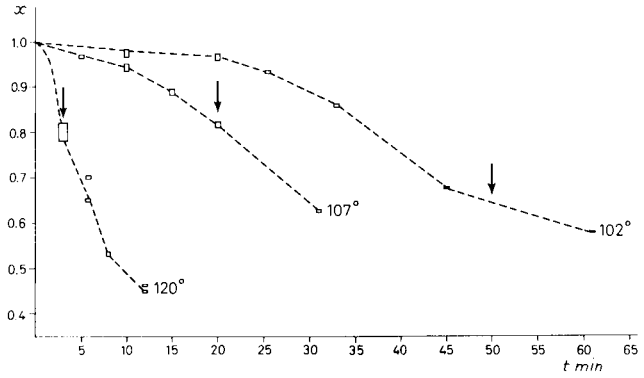


Fig. 1. Kinetics of the thermal isomerization of the *O,N,N*-trimethyl ester, IV, before and after melting. The arrows show the melting time of the samples. The data on the melt at 120° were used for evaluating an approximate rate constant.

section, will help to make these points clear. As is apparent, the reaction in the solid phase proceeds at a rate and with a mechanism significantly different from that in the molten phase: it is slow at the beginning and accelerates in time at 102° and again at 107°, but at 120°, when the samples melt within 2-3 minutes, about 20% of the product has been transformed. Using these latter results to estimate the order of magnitude of the rate constant, one obtains $(2 \pm 1) \cdot 10^{-3}$ mol^{-1} sec^{-1}, which is comparable with the rate constants found with TT at 225° and 238°, more than one hundred degrees higher.

Consequently, we believe that the assumption of a much higher conversion rate of the intermediates with respect to TT at the same temperature is sufficient for the sake of the present discussion.

It was, however, more important to prove that the mechanism operated as assumed. One significant point in this respect was the observation, mentioned above, that the conversion of the first intermediate, after melting, takes place stepwise, because the reaction mixture contains both the second intermediate and the final product. More detailed data are given in the experimental section.

A more accurate analysis of the conversion mechanism was carried out on X_2, this compound being more convenient because it transforms, in one step, into a single known product. For this purpose the deuterium labelled *O,N,N*-trimethyl ester described in the previous section, whose main fraction (91.1%) had the isotopic composition (OCD_3, NCH_3, NCH_3), was melted with varying amounts of O^{18}-labelled (OCH_3, NCH_3, NCH_3). This latter was prepared by reacting methyl iodide with the O^{18}-labelled TT described in the previous paper (2). The mass spectra analysis of the reaction mixture, based on the intensity of the molecule-ion peak, was carried out as follows. Let m and M be the average molecular weight and g and G the amounts of the *O,N,N*-trimethyl esters labelled with D and with O^{18}. The mole ratio of mixing is then $\lambda = m\,G/g\,M$ and the mole fraction of the various isotopic molecules before the reaction, based on the known composition of these materials, is as follows:

$(O^{16}CH_3, NCH_3, NCH_3)$	$(O^{16}CD_3, NCH_3, NCH_3)$
171	174
$a/(1+\lambda)$	$b/(1+\lambda)$
$(O^{16}CD_3, NCD_3, NCH_3)$	$(O^{18}CH_3, NCH_3, NCH_3)$
177	177
$c/(1+\lambda)$	$\lambda x/(1+\lambda)$

Here x (=0.825) is the fraction of molecules which are labelled with 3-O^{18}, as determined in the preceeding paper (2). The mole fractions of methyl groups available in the process are $(\lambda x+a)/(1+\lambda)$ for CH_3 and $(b+c)/(1+\lambda)$ for CD_3. If one takes into account that a fraction δ of each isotopic species might be converted by an intramolecular reaction, (there is evidence of this occurring in the solid phase before melting), then the mole fraction of each species taking part in the intermolecular reaction must be multiplied by a factor $(1 - \delta)$.

The mechanism assumed in eqs. *(9)-(12)* corresponds to a statistical distribution of the methyl groups among the different isotopic residues, $C_5H_6N_3O_3$, with masses 156, 159 and 162, whose mole fractions are, respectively, $(a+b)\ (1-\delta)/(1+\lambda)$, $c(1-\delta)/(1+\lambda)$ and $\lambda x(1-\delta)/(1+\lambda)$. By

addition of a CH_3 or of a CD_3 group they form TTET molecules with masses 171, 174, 177 and 180 in amounts which are proportional to the product of the mole fractions of the combining species. Summing for each mass the inter- and intramolecular contributions, f_m' and f_m'', the probability normalization factor is

$$N = \Sigma_m (f_m' + f_m'') = (1-\delta+\delta^2)(1+\lambda x)/(1+\lambda) \qquad (24)$$

and the predicted peak intensity for each mass is then given by $I_m = (f_m' + f_m'')/N$. A simplified expression for these observables can be used in the present case because, as will be seen, δ is so small that δ^2 can be neglected in eq. *(24)*. Moreover, δ is comparable to the observed values of a and c, and therefore the contribution to the intensity of terms δa and δc is also negligible. Remembering that $a+b+c = 1$, the exact I_m can be replaced by the following approximations, in which the inter- and intramolecular contributions to the peak intensity have been separated.

$$I_{171} \simeq (\lambda+a)(1-c-\delta b)/(1+\lambda)(1+\lambda x),$$

$$I_{174} \simeq (b+\lambda c)(1-\delta)/(1+\lambda)(1+\lambda x) + \delta b/(1-\delta)(1+\lambda x),$$

$$I_{177} \simeq [c+\lambda x(\lambda+a)(1-\delta)]/(1+\lambda)(1+\lambda x) + \delta\lambda x/(1-\delta)(1+\lambda x), \qquad (25)$$

$$I_{180} \simeq \lambda x(1-a-\delta)/(1+\lambda)(1+\lambda x).$$

These equations allow one to predict the peak intensities from the known isotopic composition of the reaction mixture (a, b, c, λ and x), once a value for δ has been chosen.

TABLE I

Molecular ions intensities (%) for mixtures of O^{18}- and D-labelled IV

m	171	174	177	180
2:1	23.2	14.6	44.3	17.9
2:1	22.6	15.6	44.4	17.3
2:1	24.2	13.9	43.6	18.3
2:1	25.0	15.1	42.0	17.8
1:1	26.0	29.1	22.7	22.2
1:1	26.4	28.6	23.9	21.0
1:1	25.9	30.1	24.1	19.9
1:1	25.5	28.2	25.0	21.3
1:2	23.5	43.0	15.3	18.2
1:2	22.2	42.1	16.2	19.5
1:2	23.1	43.9	14.2	18.8
1:2	24.0	42.1	16.2	17.7

When δ is taken as zero the fitting is rather rough. Another possibility is to obtain δ by equating I_{171} or I_{180} to the observed intensity obtained with a single mixture (or a given λ value) and using it for all the others. And this procedure was adopted. However, due to the errors inherent in the measured intensities, δ itself is subject to large errors because it is derived as the small difference between two much larger quantities.

The experimental data are collected in Table I. Working with mixtures of O^{18}- and D-labelled molecules in the approximate ratios 2:1, 1:1 and 1:2, the δ's obtained from the fitting of I_{171} were, in the same order, 0.051, 0.072 and 0.094 while those from I_{180} were 0.087, 0.006 and 0.002. The calculated intensities were all based on $\delta = 0.05$ and are compared with the observed ones in Table II. The agreement is certainly satisfactory and

TABLE II

Comparison of calculated and observed molecular ion peak intensities for mixtures of O^{18}- and D-labelled IV (a)

	2:1		1:1		1:2	
m	calc.	obs.	calc.	obs.	calc.	obs.
171	23.8	23.8	26.5	26.0	24.2	23.2
174	13.5	14.8	29.3	29.0	44.4	42.7
177	44.1	43.6	24.0	23.9	13.8	15.5
180	18.6	17.8	20.1	21.1	17.6	18.5

(a) Calculated from eq. *(25)* and observed as average of data in Table I.

definitely indicates that the conversion of the molten X_2 to TTET takes place by an intermolecular process as predicted: this is confirmed by the presence of isotopic molecules with mass 180 and by the fact that their peak intensity and that of the 171 isotope change as predicted by eq. *(25)*. The intramolecular process is of minor importance, and mainly related to the conversion taking place in the solid material before melting.

These results also give further proof of the accuracy of the isotopic composition deduced from the mass spectra of the material obtained by the reaction of methyl iodide with CD_3-labelled TT, as reported in the preceeding section.

THE ROLE OF SUBSTITUTIONAL SYMMETRY

About forty years ago Slotta and Tschesche (9) tried to obtain the *O,O,N*-trimethyl ester of cyanuric acid by reacting *O,O*-dimethylcyanuric acid with diazomethane. As reported above they failed to recognize the presence of the desired *O,O,N*-ester and believed that the reaction

only led to the formation of TT. At the same time they tried to obtain the *O,N,N*-trimethyl ester by reacting methyl iodide with the silver salt of the *N,N*-dimethyl cyanuric acid and found the reaction product to be TTET. They therefore proposed a "principle of symmetry", to account for the supposed tendency of cyanuric acid to form only symmetric esters. This interpretation, which has been credited in the recent literature (3), seems to be disproved by the findings reported above.

There is, however, a very large difference between the thermal stability of the *O,O,N*- and *O,N,N*-trimethyl esters on one hand, and that of TT on the other, which remains to be explained. This is not an isolated observation, because a similar situation arises with the methyl derivatives of trithiocyanuric acid (11). Its *S,S,S*- and *N,N,N*-trimethyl esters remain unchanged up to 260°, but the *S,S,N*- and *S,N,N*-trimethyl derivatives isomerize, after melting, into the symmetrically substituted compounds.

The question then arises of the role of substitutional symmetry in determining the thermal stability of these molecules, which, when the equivalent positions of the molecule are equally substituted, undergo the same basic reaction at a much higher temperature. An attempt has been made to solve this problem by studying the electronic structure of the involved molecules. These have a molecular core of nine centres with twelve π-electrons whose total energy and distribution change as a consequence of the different valence state of the nitrogen and oxygen atoms in the various tautomeric forms. The planarity of I and II has been established by x-ray diffraction (4), and the other structures have also been assumed to be planar.

The following calculations were carried out according to the Pariser-Parr-Pople approximation of the A.S.M.O., S.C.F. method. The interaction of the π-electrons with the methyl groups and the lone-pair electrons was limited to the inclusion of the penetration integrals in the core terms. The calculation of the lower excited energy levels was based on all the singly excited configurations. The remainder of the procedure was the same as that described in a previous paper (12), and a more complete account will be given elsewhere.

In order to have a measure of the reliability of the calculated wave-functions and eigenvalues, the lowest calculated singlet-singlet and singlet-triplet transitions were compared with the observed absorption spectra. The agreement, in Table III, is very satisfactory when the penetration integrals are neglected, but is not as good when these terms are included. This is not surprising in itself, as the limited π-core interaction which was used is more appropriate for the description of the ground state than the excited one. We shall therefore discuss, because they are better in principle, the electron distribution and ground state energy calculated with the inclusion of penetration terms, adding the proviso that the other set would allow one to reach the same conclusions.

TABLE III

Comparison of observed lowest $\pi\rightarrow\pi^*$ absorption band with calculated electronic transitions (ev)

Me-ester	Observed	Ref.	1^{st} S→S		1^{st} S→T	
			(a)	(b)	(a)	(b)
O,O,O	≃6.3	17	6.26	5.50	5.43	4.09
O,O,N as.	5.43	10	5.50	4.70	4.14	2.87
O,O,N sym.		–	4.60	4.07	3.46	2.53
O,N,N	5.64	6	5.61	5.11	3.95	2.70
N,N,N	>6.5	17	7.08	6.54	4.39	3.16

(a) without, and (b) with, the inclusion of penetration integrals.

The total energy gain of the π-electrons when they are bound into the molecular core is given by

$$E_\pi = \sum_i (\epsilon_i + I_i) - \Sigma_k n_k W_k \qquad (26)$$

where $I_i = (\psi_i|H|\psi_i)$, ϵ_i is the eigenvalue corresponding to the M.O. ψ_i, and the i-summation is carried out over the occupied M.O.'s; n_k is the number of π-electrons associated with the k^{th} centre, W_k its valence state ionization potential, and the k-summation is carried out over all the core atoms. The data collected in Table IV show clearly

TABLE IV

Total π-energy gain for the different esters (ev)

Me-ester	E_π, eq. *(26)*	relative ΔE_π	ratios
O,O,O	- 354.6	53.9	0.868
O,O,N as.	- 371.2	37.3	0.909
O,O,N sym.	- 373.2	35.3	0.913
O,N,N	- 387.4	21.1	0.948
N,N,N	- 408.5	0	1

that the molecular core corresponding to TTET gives the largest binding energy for the π-electrons, and qualitatively justifies the conversion of the other molecules to the most stable structure. The rate at which the reaction takes place cannot, however, be related to the trend calculated for E_π. This rather suggests that the reaction would be fastest with the isomer giving the largest energy gain, although in all cases one would expect a comparable order of magnitude. Therefore E_π cannot be related to the activation energy of the process.

This energy, according to eq. *(23)* of our model, includes the energy of dissociation of the neutral molecule into an anion and the cation Me^+. A calculated quantity which can be related to this process is the dipole moment. Its calculated values, collected in Table V, were obtained

TABLE V

Calculated dipole moments (*D*) for the mixed esters

Me-ester	μ_t	μ_σ	μ_π
O,O,N as.	5.24	0.38	5.20
O,O,N sym.	8.06	0.28	7.78
O,N,N	5.63	0.36	5.66

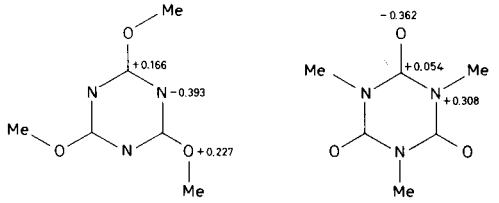


Fig. 2. Net π-charge diagrams for the symmetric *O*- and *N*-esters.

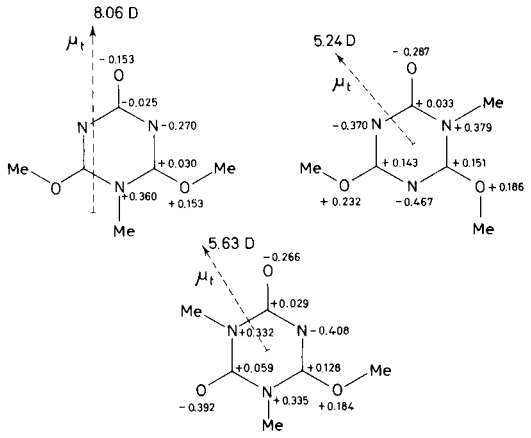


Fig. 3. Net π-charge diagrams and total dipole moments for the mixed *O*- and *N*-esters.

from the π-electron distributions shown in Fig. 2 & Fig. 3 and from standard σ-bond moments taken from the literature (13). It is evident that the non-symmetrically substituted molecules are strongly polar, and it is indeed reasonable to expect that the same ionic dissociation process for polar tautomers in a polar medium, such as their own liquid state, will take place at much lower temperatures.

This conclusion also qualitatively correlates our observations with the electronic structure of the molecules, and it is the simplest explanation that can be proposed at the present time.

DISCUSSION AND CONCLUSIONS

The assumptions implied in the proposed mechanism and those made in the discussion above have been found to agree with the experimental observations.

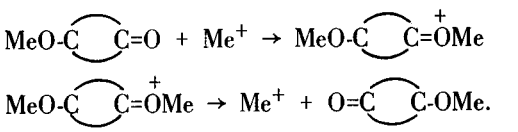
The process has been shown to be stepwise, particularly for the conversion of the first intermediate X_1 into a mixture (X_2 + TTET) which is eventually transformed into the same single product as that obtained from the overall reaction.

The ionic nature of the process also seems to be established beyond doubt: the exchange of H^+ with Me^+, which occurs with all the OMe derivatives concerned, proves that all these molecules are able to release Me^+ ions. Whether this happens before the molecules themselves are attacked by H^+, or afterwards, is a debatable point. However, the second of these possibilities seems the most likely, because the singly protonated species, *N,N*-dimethylcyanuric acid, is the only reaction product in all cases.

The remaining important question is whether the dissociation reaction, corresponding to eq. *(1)* of our mechanism, occurs with free diffusion of the ions in the liquid. It is difficult to believe that such a crude scheme can represent the real situation, because the mean free path of Me^+ is small, and that of the anions is even smaller. It is possible that the redistribution of the Me groups among the different molecules can only take place at very short distances. The Me^+ ions are most likely captured by neighbouring molecules, and they are unlikely to travel further than their next neighbours. The very fast conversion of the intermediates can thus be regarded as a chain propagation of steps between several neighbouring molecules once the first one has occurred. The slowing down of the overall reaction, after 2/3 conversion, at a rate higher than the 2^{nd} order and the small intramolecular reaction observed in the transformation of X_2 to TTET, are both indications that the diffusion of Me^+ is limited to very short distances.

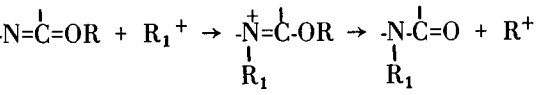
The data obtained for the reaction in the molten state do not directly prove that the role of Me^+ is the one assumed in eq. *(2)*. However, the study of the reactions in solution has established that the attack of the Me^+ ions on the neutral molecules is the elementary process which starts the tautomeric isomerization of the dissolved molecules. In this respect it has at least been possible to show that the step assumed to occur in the molten liquid is possible and is effective in the manner proposed. A small part of the reaction in solution is due to an intramolecular rearrangement, which can be regarded as ionic and

shows some kind of "cage effect" preventing the diffusion of Me^+. Even more interesting is the exchange reaction of Me at the OMe groups. This is apparently independent of the tautomeric isomerization, because it is also observed when the X_2 intermediate, the final product of the reaction under those conditions, is dissolved in methyl iodide. The more likely mechanism seems to be



An exchange process of this type is also possible in the molten state, but further experiments are required to decide its role in the reaction studied above.

The results obtained so far lead one to the more general conclusion that the tautomeric isomerization of the N-C-OR system begins when a nitrogen atom is attacked by a cation:



where R and R_1 are H or Me. The driving force for this process is the greater stability of the amido structure, due to the energy gain arising from the valence state change of *N* and *O* and the consequent redistribution of the electrons in the molecular core. This energy gain certainly depends on the particular balance of the interaction between the *N* and *O* atoms through the *C* interposed in the chain, and is peculiar to the N-C-O system, because the replacement of *O* by *S* results in somewhat different behaviour. While postponing further discussion to another paper on the esters of trithiocyanuric acid, it is important to stress here that cyclic systems such as those studied above allow one to carry out a detailed analysis of the role of the π-electrons that is independent of the σ-frame. The polarity of the intermediate *O,O,N*- and *O,N,N*-esters is in fact due almost entirely to the π-electrons because the σ-component of the dipole moment is largely cancelled out by the core symmetry, while the contribution of the Me groups is never larger than about 10%. Of course, in the actual case of the molecules in the solution or in the melt, this conclusion only holds to a first approximation. The average position of the Me groups of OMe esters may not be in the ring plane, as was assumed in our calculation, and consequently even the symmetrically substituted OMe ester will undergo an orientation polarization which should favour the dissociation step. The measurement of the dipole moments of these compounds and of their dependence on temperature should allow one to obtain a more quantitative idea of this phenomenon.

The data available at the present time do not give any information on the energetics of the various steps. In order to study this aspect it will be necessary to establish the temperature dependence of the rate constants, but there are considerable technical difficulties in controlling the various factors affecting the reaction. We hope to report on these aspects in the near future.

EXPERIMENTAL

Thermal Isomerizations.

The thermal isomerization reactions were carried out in a sealed tube immersed in a controlled temperature bath. Melting points (uncorrected) were also observed in a sealed capillary.

O,O,N-Trimethyl Ester of Cyanuric Acid (V).

The sample was put into the bath at 105° (the m.p. reported by Hantzsch and Bauer (8)) and the temperature raised by about 1° every 5 seconds: in this case the observed m.p. was 142-144°. However, if the starting temperature was 138°, the melting occurred at 147-149°. The molten material was a mixture of II, IV and the starting product.

Samples kept in the bath at 148° for increasing lengths of time transformed into mixtures with the following compositions

after	3 min:	25% II, 52% IV, 23% V
after	10 min:	80% II, 10% IV, 10% V
after	30 min:	complete transformation into II.

Heating at 160° or 175° for 8 minutes gave reaction mixtures which still contained small residual amounts of V, but no IV.

The composition of each mixture was established by comparison of its IR spectrum in carbon tetrachloride solution with that of mixtures of known composition. Details of the procedure are given below.

O,N,N-Trimethyl Ester of Cyanuric Acid (IV).

The residual amount of IV in a reaction mixture was determined by recording its optical density in an aqueous solution at 230 mμ (14). The listed values are the averages of three spectral recordings. The molar extinction coefficient was $\epsilon_{230} = 3600 \pm 100$. The interference of II on the optical density (1 cm), at the chosen wave-length, was less than 0.005 for a sample of 3 mg., 90% transformed. The data at 102, 107 and 120°, collected in the following table, give, respectively, the time in minutes and the initial and residual amounts of IV in mg.:

102°	10	20	28	33	45	61
	2.235	2.555	2.955	3.495	3.695	1.735
	2.158	2.479	2.764	3.002	2.496	1.003
107°	5	10	15	20	31	
	2.375	3.100	2.650	2.530	2.310	
	2.301	2.932	2.347	2.066	1.442	
120°	6	6	8	12	12	16
	3.025	3.310	2.600	3.275	2.765	3.050
	2.117	2.151	1.376	1.528	1.239	0.792

The average transformation of the samples kept at 120° until melting, which required from 150 to 200 seconds was about 20%. The heating of the solid prior to melting is the variable most difficult to control and responsible for the large scatter of the data.

Reactions with Methyl Iodide.

Reactions with methyl iodide were carried out in a tube which had been sealed in a vacuum line after removing the air by repeated freezing of the material with liquid nitrogen. This procedure avoided contamination through oxidation by the residual air. The excess methyl iodide was 50 to 100 moles/mole. Acetone, benzene, *iso*-octane, dioxane, and ethyl acetate were also added in some cases in the ratio from 1:1 to 3:1 per volume methyl iodide. The reaction product was obtained after evaporation at room temperature, and also at reduced pressure when necessary. When the reaction was carried out at 100° for 12 hours the product obtained from I was always very pure IV. When the temperature was raised to 180° for 24 hours (caution: 20 atms pressure), the reaction product was II. A mixture of IV and V, together with the starting compound I, was obtained when the reaction was carried out at room temperature for 2 weeks.

Partial isomerizations were also observed when a small amount of methyl iodide was used in an excess of solvent and kept at 100° for 12 hours. Thus 150 mg. I + 400 mg. methyl iodide, dissolved in 2 ml. of solvent, gave mixtures of the following composition:

(a) in benzene: 50% I, 25% IV, 25% V
(b) in ethyl acetate: 45% I, 45% IV, 10% V.

The compositions were established by comparison of their IR spectra with those of mixtures of known composition, as described below.

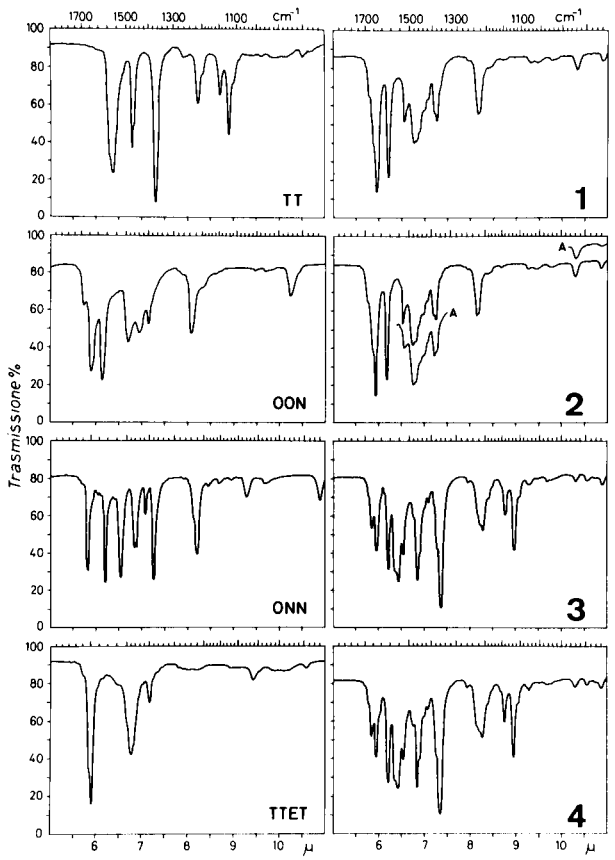


Fig. 4. I.R. absorption spectrum in the range 5-11 μ:
(a) pure components I (TT), II (TTET), IV (ONN) and V (OON), in carbon tetrachloride solution, concentration from 0.5 to 1.0% w/w;
(b) *1:* reaction mixture obtained by melting V, 3 minutes at 148°; *2:* synthetic mixture formed by 25% II, 52% IV and 23% V; *3:* reaction mixture from 150 mg. I + 400 mg. methyl iodide in 2 ml. benzene; *4:* synthetic mixture 50% I, 25% IV and 25% V.

The lines labelled A in the plot *b-2* belong to a mixture made by 27% II, 56% IV and 17% V and are shown as a measure of the accuracy of the present procedure.

Composition of Reaction Mixtures.

Although our aim was only to obtain qualitative evidence for the presence of the intermediates IV and V, we thought it significant to establish the order of magnitude of their relative concentrations.

The composition of several reaction mixtures was therefore measured by comparing their IR spectrum with that of sample mixtures of known composition. We have dealt with two types of reaction mixtures: those obtained from thermal isomerizations, containing II, IV and V; and those from the methyl iodide solution isomerization containing I, IV and V. The spectra of the pure products, in Fig. 4a, show that in both instances there are absorption bands which characterize each component of the mixtures. Two typical examples of matching spectra are also shown in Fig. 4b.

The spectra were recorded on a Beckman IR-5 instrument, in carbon tetrachloride solutions, 0.1 mm cell thickness.

Methylation in Molten Liquids.

Methylation reactions were carried out by melting a 1:1 mole mixture of the carboxylic acid with any one of the *O*-methyl derivatives I, IV or V, and keeping the melt at about 200° for 20-45 minutes. The methyl ester of the acid was distilled off by condensation at reduced pressure on a cold point (liquid nitrogen). The yield was always more than 90% of a very pure material, which was identified by comparing its IR spectrum with that of an authentic sample prepared from the acid with diazomethane. The other reaction product was *N,N*-dimethyl cyanuric acid (III), identified in the way described below. A small amount of II was occasionally found to be present. Benzoic, salicylic, anisic and phenylacetic acids were used.

Hydrolysis of the Mixed Esters IV and V.

The esters were dissolved in concentrated hydrochloric acid, the solution left to evaporate on a *bain-marie*, and the residue crystallized from ethanol and identified as follows.

N-Methylcyanuric Acid.

This was obtained from the hydrolysis of V, m.p. 290° (lit. 285-286° (15), 275-285° (16)).

Anal. Calcd. for $C_4H_5N_3O_3$: C, 33.6; H, 3.5; N, 20;4. Found: C, 33.5; H, 3.5; N, 28.8.

N,N-Dimethylcyanuric Acid.

This was obtained from the hydrolysis of IV, m.p. 220° (lit. (9) 222°), identified by mixed m.p. and comparison of its IR spectrum with an authentic sample synthesized from *N*-methylurea according to Slotta and Tschesche (9).

Reactions with Labelled Products.

O^{18}-Labelled IV was obtained by reacting methyl iodide with

the O^{18}-labelled I described before (2). Its average mol. weight was 176.3. *D*-Labelled IV was prepared by reacting methyl iodide with the fully deuterated I described before (2). Its average mol. weight, calculated from the isotopic composition given in Table I, was 173.8.

Mixtures of the above labelled products were prepared by dissolving them in carbon tetrachloride and evaporating the solutions. Isomerizations were carried out by heating the molten material at 135° for 20 minutes. The following mixtures were prepared (O^{18}- + *D*-labelled): mg. (4.590 + 2.270), $\lambda = 1.993$; mg. (3.385 + 3.640), $\lambda = 0.9167$; mg. (2.335 + 4.485), $\lambda = 0.5132$.

Mass Spectra.

The mass spectra were recorded on C.E.C. mass spectrometer Model 21-110 B, under conditions corresponding to a resolving power of 1:3000. The ionization energy for recording the molecular ion peak intensity was 12 ev and the vaporization temperature 50 to 70°.

The ions observed in the mass spectrum of IV (ionization energy 70 ev) are listed below with their relative intensity and a tentative identification based on the isotopic spectrum of IV-(OCD_3) and on the spectra given in the previous paper (2).

m/e	relat. int.	identification
28	1	
29	1	
30	3	
41	1	$CHN_2 + C_2H_3N$
42	1.5	$C_2H_4N + CNO$
43	2	$CHNO$
44	1	CH_2NO
56	38	$C_3H_4O + C_2H_2NO$
57	5	C_2H_3NO
58	9	C_2H_4NO
70	3	C_2NO_2
72	4	$C_2H_4N_2O$
83	5	
84	50	$C_3H_2NO_2$
85	3	isotopic
86	3	
96	2	
99	58	$C_3H_3N_2O_2$
100	3	isotopic
113	7	$C_4H_5N_2O_2 + C_4H_3N_3O$
114	23	$C_4H_6N_2O_2 + C_4H_4N_3O$
115	9	$C_4H_7N_2O_2 + C_4H_5N_3O$
127	1	
128	2	$C_4H_6N_3O_2$
129	1.5	
138	16	$C_5H_4N_3O_2$
156	32	$C_5H_6N_3O_3$
157	20	$C_5H_7N_3O_3$
158	3	$C_5H_8N_3O_3$
171	100	$C_6H_9N_3O_3$
172	8	isotopic
173	1.5	isotopic

The main features of the isotopic spectra of IV-(OCD_3) are the unchanged peaks at *m/e* 56, 57, 58, 70, 128 (ions which contain NCH_3 groups (2)) and the shifts 72 → 75 (OCH_3?); 84 → 85; 99 → 100; 138 → (140, 141); 156 → (157, 158). These data were not analyzed further because the main interest was in the molecular ion intensities.

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REFERENCES

(1) L. Paoloni and M. L. Tosato, *Ann. Chim.* (Rome), **54**, 897 (1964). (Part III.)

(2) L. Paoloni, G. Nencini, M. L. Tosato, T. Salvatori, *Gazz. Chim. Ital.*, **97**, 635 (1967). (Part V.)

(3) E. M. Smolin and L. Rapoport, "*s*-Triazine and Derivatives," Interscience Publishers, Inc., New York, 1959, p. 74.

(4) A. Vaciago, private communication.

(5) L. Paoloni and M. L. Tosato, *Ric. Sci.*, **37**, 258 (1967).

(6) M. L. Tosato and L. Paoloni, *ibid.*, **37**, 259 (1967).

(7) E. Bilmann and J. Bierrum, *Ber.*, **50**, 503 (1917).

(8) A. Hantzsch and H. Bauer, *ibid.*, **38**, 1005 (1905).

(9) K. H. Slotta and R. Tschesche, *ibid.*, **60**, 301 (1927).

(10) L. Paoloni and M. L. Tosato, *Ric. Sci.*, **38**, in press.

(11) M. L. Tosato and L. Paoloni, *J. Chem. Soc.* (C), 909 (1966).

(12) M. Cignitti and L. Paoloni, *Theor. Chim. Acta* (Berlin), **7**, 383 (1967).

(13) See, *e.g.*, L. Paoloni and A. G. Giumanini, *Gazz. Chim. Ital.*, **96**, 291 (1966).

(14) The cooperation of Dr. Patrizia Sassoli in carrying out these measurements is gratefully acknowledged.

(15) E. Fisher and F. Frank, *Ber.*, **30**, 2604 (1897).

(16) W. Close, *J. Am. Chem. Soc.*, **75**, 3617 (1953).

(17) M. Cignitti and L. Paoloni, *Spectrochim. Acta*, **20**, 211 (1964).

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