Thermolysis of *cis*- and *trans*-1,2-Dideuteriocyclobutane

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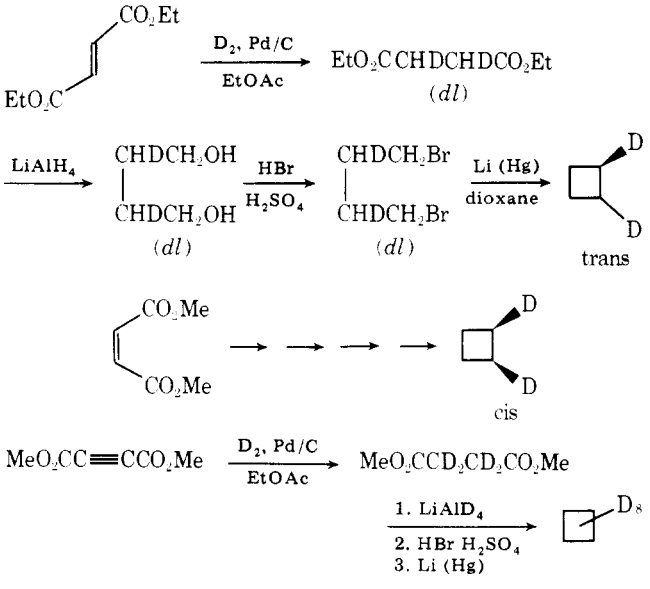
The synthesis and stereochemistry of thermolysis of *cis*- and *trans*-1,2-dideuteriocyclobutane is reported and the results are compared to previously calculated models of tetramethylene. Cis–trans isomerization of dideuteriocyclobutane and complete cis–trans isomerization of ethylene-d_2 were observed. The fragmentation/isomerization ratio of 3.0 obtained at low fractional isomerization is consistent with a potential energy surface for tetramethylene, which is symmetric with regards to fragmentation and recombination. The rapid methylene rotation necessary to explain the observed stereochemical features of the reaction also limits the magnitude of the "through-bond coupling" interaction to a value comparable to the magnitude of the potential energy well.

The thermal dissociation of cyclobutane to form ethylene has widely been held to be a nonconcerted process proceeding by way of tetramethylene. The most convincing experimental support of this view is the observed loss of stereochemical integrity of the recovered reactant.[1] In addition the olefinic products isolated have generally been extensively isomerised,[1] although exceptions have been reported.[2] The presumed intermediacy of tetramethylene derivatives in this and other orbital symmetry forbidden reactions have raised the question of whether this intermediate is best represented by a minimum in the potential energy surface or as a large energetically flat surface near or at the transition state. Hoffmann, Swaminathan, Odell, and Gleiter[3] using extended Hückel calculations have reported two minima in the potential surface for tetramethylene, a gauche and a trans form, but found these conformations to be unstable with regards to fragmentation to ethylene. These authors found a large region of coordinate space where the energy of tetramethylene did not vary much with respect to torsional or bending degrees of freedom. The term "twixtyl" was suggested for such a species. More recently, Segal[4] has reported results of ab initio calculations on tetramethylene. Although qualitatively in accord with the extended Hückel calculations, a discrete minimum was observed in the surface separating ethylene and cyclobutane. In view of the continued interest in such symmetry forbidden reactions, we have prepared *cis*- and *trans*-dideuteriocyclobutane and have examined the stereochemical consequences of the thermolysis reaction on reactants and products. Our results have been compared to those expected of simple models of tetramethylene, constructed from the potential surfaces of Segal and Hoffmann et al. and the empirical estimates of Beadle, Golden, King, and Benson.[22]

cis- and *trans*-dideuteriocyclobutane were prepared according to the scheme outlined below in 40% overall yield. The cyclobutanes contained 5% butane. The diasteriomeric cyclobutanes were analyzed by their infrared spectra, which were very similar to cyclobutane, their mass spectra which gave parent ions of *m/e* 58, and by quantitative conversion to an isotopic mixture of ethylenes. The ethylenes were identified by comparison to a mixture of authentic samples obtained commercially or synthesized.[6] A portion of the infrared spectra which permitted discrimination between stereoisomers is reproduced in Figure 1. A comparison of these spectra shows the trans compound to be stereochemically homogeneous. The cis compound appears to be contaminated with some trans. This conclusion is further supported by the thermolysis results.

The thermolysis of cyclobutane was studied in both flow and static systems. The reaction was shown to be homogeneous in these vessels by demonstrating that the isotope effect k_{H8}/k_{D8} was pressure dependent[7] (see Experimental Section). However, control experiments indicated that even at 380 °C, *cis*- and *trans*-dideuterioethylene were extensively isomerized

Scheme I



in the static experiments. We believe this to be partially due to the Pyrex surface used and partly due to traces of oxygen.[8] These results dramatize the need for experimentalists to demonstrate stereochemical integrity rather than to assume it when dealing with such systems. Isomerization was severely curtailed in a flow system (quartz tube) using nitrogen as a carrier and completely eliminated in the absence of a carrier gas.

The cis–trans composition of ethylene obtained from the thermolysis of *cis*- and *trans*-dideuteriocyclobutane is given in Table I. The first column lists the relative intensities of cis to trans while the other entries relate band ratios to the most abundant ethylene present, monodeuterioethylene. As indicated, within experimental error, complete isomerization of the olefin was observed. These results are similar to those obtained by Scrinivasan and Hsu in the thermolysis of *c*-1,*c*-2-dideuterio-*t*-3,*t*-4-dimethylcyclobutane.[1e]

The composition of the recovered starting material is shown in Table II. A fragmentation/isomerization ratio of 3.0 was obtained for the trans compound, while the ratio obtained by the cis compound varied but remained above 3.0. The results obtained were analyzed on the assumed intervention of tetramethylene, either as a "twixtyl" or as an intermediate. The kinetic expressions used in this analysis are shown in Schemes II and III. Isotope effects were neglected and rapid methylene rotation assumed in both cases. The "twixtyl" was treated as a long-lived transition state which could recyclize or fragment; each was considered equally probable. The fate of the tetramethylene intermediate was determined by the potential surface calculated by Segal and relative rates were estimated

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Table I. A Comparison of the Relative Intensities of Infrared Bands (cm^{-1}) of *cis* (C), *trans* (T) Dideuterio and Monodeuterioethylene (M) Produced at 380 and 500 °C

ethylene production conditions[a]	dideuterio-cyclobutane	ethylene band ratios 843(C)[d]/987(T)[e]	987(T)/942(M)[f]	843(C)/807(M)
no isomerization, pressure <1 mm (3% reaction, 500 °C)	cis[b]	0.64 ± 0.01	0.72 ± 0.01	0.87 ± 0.01
	trans[c]	0.63 ± 0.02	0.76 ± 0.02	0.86 ± 0.02
isomerization 12%, 225 mm N_2 pressure (20% reaction, 380 °C)	cis	0.62 ± 0.01	0.74 ± 0.01	0.88 ± 0.03
	trans	0.63 ± 0.01	0.73 ± 0.01	0.90 ± 0.02
complete isomerization (variety of conditions)	cis	0.61 ± 0.02	0.74 ± 0.02	0.86 ± 0.01
	trans	0.63 ± 0.01	0.76 ± 0.01	0.90 ± 0.02

[a] This column describes the extent of isomerization of ethylene as a function of conditions in separate control experiments. [b] Registry no. 68344-07-0. [c] Registry no. 68378-61-0. [d] Registry no. 2813-62-9. [e] Registry no. 1517-53-9. [f] Registry no. 2680-00-4.

Table II. Results from the Thermal Decomposition of 1,2-Dideuteriocyclobutane

run	temp,[a] °C	added N_2, mm	initial cyclobutane, mmol	recovered cyclobutane, mmol	recovered ethylene, mmol	% fragmentation[c]	% isomerization	fragmention/isomerization
				trans-Dideuteriocyclobutane				
1	380	225	0.562	0.222	0.661	59.7 ± 0.8	21 ± 3	2.8
2	380	225	0.608	0.346	0.467	40.7 ± 2	14 ± 3	2.9
3	380	225	0.484	0.329	0.293	31.2 ± 1	11 ± 3	2.8
4	550	145	0.914	0.26	1.33	72.1 ± 0.6	23 ± 3	3.1
5	550	153	0.594	0.128	0.945	79 ± 0.5	26 ± 3	3.0
6	550[b]		0.507	0.468	0.022	5 ± 3	1 ± 1	
7	585[b]		0.507	0.360	0.209	25 ± 5	8 ± 3	3.1
				cis-Dideuteriocyclobutane				
8	380	225	0.749	0.369	0.645	46 ± 3	11 ± 2	4.2
9	550	153	0.897	0.163	1.48	79.6 ± 3	16 ± 2	5.0
10	500	224	0.495	0.360	0.245	26 ± 1	8 ± 2	3.3
11	590[b]		0.306	0.264	0.0731	12.8 ± 1	2 ± 2	

[a] Temperature control ±5 °C. [b] Total pressure <1 mm. [c] Average of recovered cyclobutane and ethylene.

Table III. Summary of the Surface Features Calculated (Segal) and Estimated Relative Rate Constants for Tetramethylene at 380 °C

feature calcd	barrier, kcal	rate constant	total fragmentation/total isomerization
E_A (gauche → trans)	3.6	k_2	
E_A (trans → gauche)	4.7	$k_{-2}(0.44\,k_2)$	
E_A (trans → 2 × ethylene)	2.3	$k_3\,(2.73\,k_2)$	
E_A (gauche → 2 × ethylene)	3.6	$k_4(k_2)$	
E_A (gauche → cyclobutane)	2.0	$k_{-1}(1.72\,k_2)$	1.44
	3.6	$k_{-1}(0.5\,k_2)$	2.48
	4.0	$k_{-1}(0.367\,k_2)$	3.4

for 380 °C (Table III). Frequency factors were assumed to cancel unless otherwise noted. A comparison to the empirical estimates of Beadle, Golden, King, and Benson is also included.

At low fractional isomerization, eq 1 and 3 can be approximated by eq 2 and 4. Summing over all possible tetramethylenes (Tables IV and V), an estimate of the fragmentation/isomerization ratio for both models can be made. A value of 2.67 was estimated for tetramethylene twixtyl whereas Segal's calculations give a value of 1.44.[21] However, as previously noted by Segal, the ab initio calculations appeared to overemphasize the stability of cyclobutane relative to two ethylenes. Thus, the barrier of 2.0 kcal for reclosure of the gauche form was estimated as a lower limit. Increasing this barrier to 3.6–4.0 kcal gives excellent but perhaps fortuitous agreement with experiment.

Empirical estimates of the barriers to fragmentation and

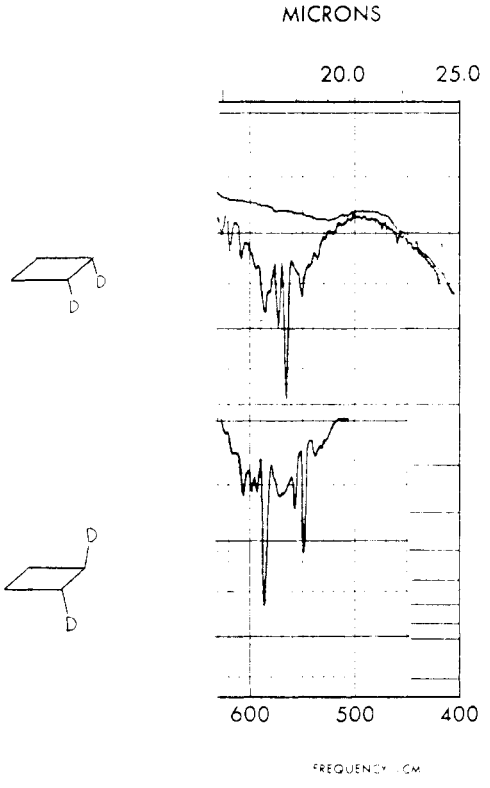
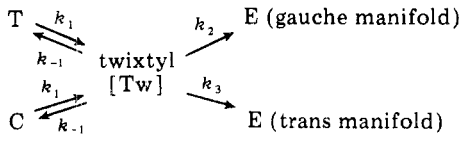


Figure 1. A portion of the infrared spectrum of *cis*- and *trans*-dideuteriocyclobutane.

recombination of tetramethylene have been reported in the literature. From arguments of strain energy and thermochemistry, Benson[10] has estimated an activation energy of 4

Scheme II. Tetramethylene Twixtyl (from *trans*-Dideuteriocyclobutane)

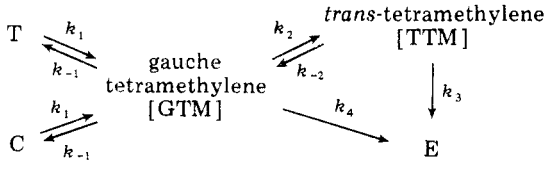


$$k_2 + k_3 = 2k_{-1}$$

$$\frac{d[E]/dt}{d[C]/dt} = \frac{(k_2 + k_3)[Tw]}{k_{-1}[Tw] - k_1[C]} \quad (1)$$

$$\Delta E/\Delta C = \frac{k_2 + k_3}{k_{-1}}; \text{ if } [C] \approx 0 \quad (2)$$

Scheme III. Tetramethylene Intermediate (from *trans*-Dideuteriocyclobutane)



$$\frac{d[E]/dt}{d[C]/dt} = \frac{k_4[GTM] + \frac{k_2k_3}{k_{-2} + k_3}[GTM]}{k_{-1}[GTM] - k_1[C]} \quad (3)$$

$$\frac{\Delta E}{\Delta C} = \frac{k_2(1 + k_3/(k_3 + k_{-2}))}{k_{-1}}; \text{ if } [C] \approx 0 \quad (4)$$

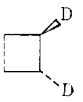
kcal for fragmentation and recombination of tetramethylene. Beadle, Golden, King, and Benson,[22] in an effort to reconcile the pressure and temperature dependence of the rate constant (their work and others), concluded a barrier of ≤6.6 kcal for recombination of tetramethylene. Using known thermochemistry, additivity methods, assigned frequencies, and other molecular parameters, the frequency factors and activation energies listed in Table VI were calculated.[23] Table VII lists the expected fragmentation/isomerization in terms of k_2' and k_{-1}'. Using the kinetic parameters listed in Table VI, a ratio of 4.4 is obtained for a recombination barrier of 6.6 kcal.[21] A barrier of about 6 kcal appears to give the best agreement.

The experimental results do not appear to rigorously distinguish between the twixtyl and the intermediate. They do support the notion that the potential surface surrounding tetramethylene is close to being symmetrical with regards to fragmentation and recyclization.

Rapid methylene rotation required by the complete loss of stereochemistry of the recovered ethylene-d_2 need not lead to the fragmentation/isomerization ratio calculated above. A conrotatory ring opening motion as proposed[24] and observed[25] for trimethylene, and/or disrotatory ring opening, would affect the ratio by eliminating tetramethylene 1 as a possible source of stereomutation of the cyclobutane ring. The maximum effect of such a possibility would be to increase all the calculated fragmentation/isomerization ratios by a factor of 1.5.

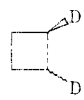
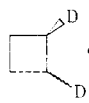
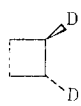
The barriers to methylene rotation are one aspect of the cyclobutane problem which theory does not seem able to estimate accurately. Hoffmann et al. calculated a barrier of approximately 12 kcal while Stephenson and Gibson[12] found that CN INDO calculations predicted an abnormally high barrier in 1,4-tetramethylene relative to methylene rotation in a butyl radical. If tunneling effects are assumed to be unimportant then our results require the barriers to methylene rotation to be comparable to those for dissociation and recombination.[13] Within the framework of Segal's calculations and the empirical estimates of Beadle, Golden, King, and Benson, this establishes an upper limit of approximately 4–8 kcal for the 1,4 through-bond coupling interaction. Rapid methylene rotation in the "twixtyl" requires this interaction to become vanishingly small.

Table IV. Fragmentation vs. Isomerization of Tetramethylene Twixtyl at 380 °C

tetramethylene (*i*)	fragmentation via (0 kcal barrier) gauche valley	fragmentation via (0 kcal barrier) trans valley	recrystallization (0 kcal barrier) cis	recrystallization (0 kcal barrier) trans
 (1)	k_2	k_3	k_{-1}	k_{-1}
 (2,3)	$2k_2$	$2k_3$	$2k_{-1}$	$2k_{-1}$
 (4)	k_{-2}	k_{-3}		$2k_{-1}$

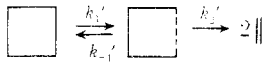
$$\sum_{i=1}^{4} \Delta E_i/\Delta C_i = \frac{4(k_2 + k_3)}{3k_{-1}} = 2.67$$

Table V. Fragmentation vs. Isomerization of *trans*-Dideuteriocyclobutane via Tetramethylene Intermediate at 380 °C

tetramethylene (i)	fragmentation via gauche conformation	fragmentation via trans conformation	cyclization cis	cyclization trans
 (1)	k_2	$k_2k_3/(k_{-2} + k_3)$	k_{-1}	k_{-1}
 (2,3)	$2k_2$	$2k_2k_3/(k_{-2} + k_3)$	$2k_{-1}$	$2k_{-1}$
 (4)	k_2	$k_2k_3/(k_{-2} + k_3)$		k_{-1}

$$\sum_{i=1}^{4} \Delta E_i/\Delta C_i = \frac{4k_2 + \frac{4k_2k_3}{k_{-2} + k_3}}{3k_{-1}}$$

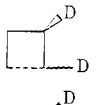
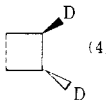
Table VI. Summary of the Empirical Surface Features Estimated for Tetramethylene[22,23] at 380 °C from *trans*-Dideuteriocyclobutane



k_i', i =	log $A_i^{\pm}$, s^{-1}	E_i, kcal/mol	total fragmentation/ total isomerization
2	13.07	8.25	
−1	12.3	6.6	4.4
−1	12.3	6.0	2.8

Conclusion. The thermolyses of *cis*- and *trans*-1,2-dideuteriocyclobutane have been investigated. The results have been interpreted in terms of a stepwise mechanism and are most consistent with the existence of tetramethylene as an intermediate with comparable barriers for fragmentation and recombination. Comparisons of observed and calculated ratios of fragmentation to recombination are in good agreement.

Table VII. Empirical Estimates of Fragmentation vs. Isomerization of Tetramethylene from *trans*-Dideuteriocyclobutane[22,23]

tetramethylene (*i*)		fragmentation	recyclization cis	recyclization trans
	(1)	k_2'	$0.5k_{-1}'$	$0.5k_{-1}'$
	(2,3)	$2k_2'$	k_{-1}'	k_{-1}'
	(4)	k_2'		k_{-1}'

$$\sum_{i,1}^{4} \Delta E_i/\Delta C_i = 4k_2'/1.5k_{-1}'$$

Table VIII. Pressure Dependence of the Kinetic Isotope Effect for the Thermolysis of Cyclobutane–Cyclobutane-d_8 at 460 °C

run	added N_2, mm	max cyclobutane pressure[a]	k_H/k_{D8} (calcd)	k_{H8}/k_{D8} (lit.[18])
		Flow system (quartz tube)		
1	87	10	1.14	1.4 (100 mm)
2	86	24	1.24	
3	85	66	1.27	
4	85	~200	1.30	
		Diffusion Stirred Flow (5 L Pyrex flask)[b]		
5		~0.08	0.965	
6		~0.08	0.974	0.8 (0.005 mm)
7		~0.015	0.85	

[a] Maximum pressure generated by replacing N_2 trap with baths at various temperatures and calculated from the Clausius Clapeyron relationship.[19] Pressure in mm of Hg. [b] Pressure generated by immersion of samples at low temperatures (measured directly).

Experimental Section

***trans*-Dideuteriocyclobutane.** Diethyl fumarate (12.2 g) was reduced in the presence of 5% Pd/C (1.0 g) in ethyl acetate (60 mL) at 1 atm pressure of deuterium gas. Evaporation of the solvent and vacuum distillation gave *dl*-diethyl succinate-d_2 (10.9 g, 88%). *dl*-Diethyl succinate-d_2 (10.4 g, 59 mmol) was reduced in refluxing ether with lithium aluminum hydride (2.43 g, 66 mmol). Hydrolysis with 2.5 mL of water, 2.5 mL of 15% NaOH, and 7.5 mL of H_2O[14] gave a granular precipitate after being stirred overnight. The precipitate was extracted repeatedly with ether. Evaporation of the ether followed by vacuum distillation afforded *dl*-1,4-dihydroxybutane-d_2 (4.22 g, 78%, bp 84–9 °C (10 μm)). *dl*-1,4-Dihydroxybutane-d_2 (4.07 g) was dissolved in a cold mixture of 48% HBr (15 mL) and concentrated sulfuric acid (10 mL). After standing overnight the mixture was heated on a steam bath (3 h). The *dl*-1,4-dibromobutane-d_2[15] which separated was washed with sodium carbonate and water, dried, and vacuum distilled. The yield was 8.45 g, 87%. *dl*-1,4-Dibromobutane-d_2 (5.43 g, 0.25 mol.) was added dropwise to a mechanically stirred suspension of lithium amalgam (0.45 g of Li, 8 g of Hg) in refluxing dioxane (20 mL).[16] *dl-trans*-1,2-Dideuteriocyclobutane (1.06 g, 73%) was isolated in the dry ice–acetone trap.

cis-1,2-Dideuteriocyclobutane was prepared in an analogous fashion. Cyclobutane-d_8 was prepared by reduction of dimethyl acetylenedicarboxylate as described above, followed by reduction with $LiAlD_4$. Similar yields were obtained except in the Li(Hg) cyclization of the dibromide. In this instance the yield of the last step was reduced to approximately 20%.

Thermolysis Experiments. The thermolysis experiments were conducted in both flow and static systems. The flow system consisted of a quartz tube surrounded by a brass sheath and heated by asbestos insulated nichrome wire. Temperature was controlled to ±5 °C. The static system consisted of a 51 Pyrex flask maintained in an air bath (±3 °C). This system contained an entrance and exit port (diameter 8 mm) and could be operated at low pressures as a diffusion-stirred flow apparatus.[17] The thermolysis of cyclobutane was shown to be a homogeneous process in these vessels by demonstrating that the kinetic isotope effect k_{H8}/k_{D8} was pressure dependent.[7] This was achieved in the Pyrex vessel by operating in the diffusion stirred flow mode. The thermolyses of *cis*- and *trans*-dideuteriocyclobutane were subsequently performed utilizing the apparatus as a constant volume system. Isotope effects for the thermolysis of cyclobutane-d_{0-8} were calculated from Benton's equation[20] for thermolysis in a flow system and from the ratio of fractional decomposition of the unlabeled and labeled material at small conversion for the diffusion stirred flow system.[17] The results are shown in Table VIII. As noted, both systems show pressure dependent isotope effects. The largest isotope effect obtained, k_H/k_D of 1.3, compares quite favorably with the literature, particularly since no attempt was made to obtain the limiting high-pressure value. The low-pressure values also agree well with previously reported values.[18]

Control Experiments. Cis–trans isomerization of ethylene was observed in the Pyrex vessel in the presence and absence of nitrogen at temperatures as low as 380 °C. Isomerization in the quartz vessel under flow conditions in N_2 was greatly retarded and completely eliminated in the absence of N_2. Thermolysis of cyclobutane in the presence of *trans*-ethylene-d_2 did not lead to trans–cis isomerization under conditions where 25% of the cyclobutane was converted to ethylene.

Analysis. The cis,trans composition of the ethylene was determined by infrared spectroscopy in a 50 mL (9-cm path) gas cell, equipped with NaCl windows. The recovered cyclobutane was analyzed in a 25 mL (9-cm path) gas cell equipped with KBr windows at pressures of approximately 150 mm on a Perkin-Elmer 337 spectrophotometer.

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Registry No.—Diethyl fumarate, 623-91-6; *dl*-diethyl succinate-d_2, 62559-63-1; *dl*-1,4-dihydroxybutane-d_2, 68344-06-9; *dl*-1,4-dibromobutane-d_2, 68344-05-8.

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(11) As noted experimentally, this approximation is somewhat poorer for the *cis*-dideuteriocyclobutane which has some trans isomer present.
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Destruction of Nitrosamines. Treatment of Nitrosamines with Various Acids and Halogens

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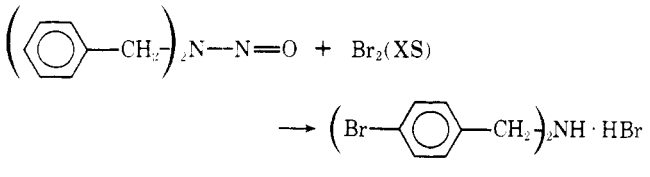
Several dinitroaniline compounds containing varying amounts of nitrosamines were treated with a variety of acids under different sets of conditions. Hydrogen chloride gas, hydrochloric acid, and hydrobromic acid were all effective at destroying the nitrosamines. Sulfuric acid efficiently removed nitrosamines without destruction, as the nitrosamines could be recovered from the neutralized acid extract. Other acids, e.g., ascorbic acid, phosphoric acid, *p*-toluenesulfonic acid, and oxalic acid, were either considerably less effective or ineffective at removing nitrosamines from dinitroaniline compounds. Additionally, molecular bromine, chlorine gas, and *N*-bromosuccinimide are quite effective in lowering the nitrosamine levels to about 1 ppm of the nitrosamine contaminant.

Nitrosamines, as a general class of organic compounds, have attracted an increasing amount of attention due to recent disclosures that many nitrosamine compounds are carcinogens in animals.[1] Recent innovations[2] in instrumentation have permitted definitive identification of nitrosamines even when present at very low levels (0.05 ppm).[3]

Since many literature references to the destruction of nitrosamines[4] deal with neat samples of the nitrosamines or materials containing relatively high amounts of the nitrosamines, we began a program to investigate the destruction of nitrosamines at the 1 → 500 ppm level. Various acids have been reported to reduce nitrosamine levels, e.g., sulfuric acid,[5] hydrogen chloride gas,[6] hydrochloric acid,[7] and hydrobromic acid.[8] However, we have found a large difference in the ability of various acids to reduce and destroy nitrosamines.

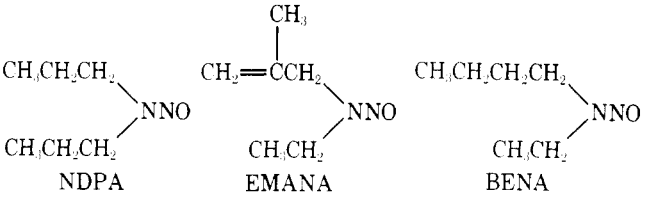
Literature also suggests that bromine[9] will react with nitrosamines. In the example cited, the author treated an aromatic *N*-nitroso compound with bromine as solvent and isolated a bromine-substituted product. This may suggest that the reactive reagent in this case is the hydrogen bromide[8] which is liberated during the electrophilic attack by bromine on the aromatic ring.



This paper details our observations that concentrated hydrochloric acid, hydrogen chloride gas, and hydrobromic acid effectively destroy low levels of nitrosamines, while sulfuric acid removes the nitrosamines by an extraction process.[10] Also, we have observed efficient destruction of nitrosamines by halogen reagents, including bromine, chlorine, and *N*-bromosuccinimide.

Results and Discussion

The specific nitrosamines analyzed for in this study were *N*-nitrosodipropylamine (NDPA), *N*-nitrosoethylmethallylamine (EMANA), and *N*-nitrosoethylbutylamine (BENA).[11] In most cases, the nitrosamines were contaminants at low levels (10–7400 ppm[10]) in various dinitroaniline solvents. The four specific dinitroanilines used include trifluralin,[12] benefin,[13] isopropalin,[14] and ethalfluralin.[15]



In the case of the acid reagents, normal reaction technique consisted of heating the dinitroaniline to approximately 70 °C (temperatures of 60–90 °C have been routinely used) and adding about 20% w/w of the desired acid relative to dinitroaniline. The reaction can be carried out neat or with an appropriate solvent (ethanol, chloroform, toluene, etc.). The reaction mixture is heated at the desired temperature for time periods of from 5 min to 3 h, with 15 min to 30 min being typical. Workup consisted of separating the aqueous and organic layers when applicable and then washing the organic layer with 10% sodium carbonate solution. Nitrosamine levels in the organic fraction were assayed by either gas chromatography,[16] combined gas chromatography–mass spectroscopy,[17] or by use of a thermal energy analyzer.[2]

Table I summarized the data generated. One can classify sulfuric acid, hydrochloric acid, hydrogen chloride gas, and hydrobromic acid as effective reagents in removing nitrosamines. In the case of hydrochloric acid, hydrogen chloride gas, and hydrobromic acid, the removal of the nitrosamine from the organic substrate is accompanied by destruction of the nitrosamine. For instance, when a sample of trifluralin containing 68 ppm of NDPA is vigorously stirred with concentrated hydrochloric acid and worked up in the usual manner, assay of the trifluralin shows <1 ppm NDPA, and assay of the methylene chloride extract of the neutralized hydrochloric acid layer shows <1 μg/mL of NDPA.

Mechanistically, hydrogen chloride gas and hydrochloric acid decomposition of nitrosamine is most probably initiated by electrophilic attack by the acid on the oxygen atom of the nitroso group,[18] a widely accepted reaction of nitrosamines.

We suggest, from preliminary data, that the chloride ion, stepwise or in a concerted fashion, attacks the nitrogen of the nitroso group resulting in nitrosyl chloride formation. This

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