(81.4% optical purity based on maximum $[\alpha]_D$ $-203.4°$), was vacuum transferred within 5 min. After 310 min, the product was withdrawn quantitatively into a receiver cooled in liquid nitrogen. Analysis and separation of the product mixture were performed as described earlier. The recovered starting material *trans*-IV had $[\alpha]_D$ $-119.7°$ (*c* 0.3816, Spectrograde cyclohexane) which corresponds to 72.3% retention of optical purity. The optical purity of the *cis*-IV was determined as usual *via* conversion to *trans*-IV, $[\alpha]_D$ $-47.4°$.

(ii) **In Acetonitrile.** A solution of (−)-*trans*-IV (20 mg), $[\alpha]_D$ $-151.5°$ (74.5% optical purity), in Spectrograde acetonitrile (0.3 ml) was heated in a thick-walled sealed Pyrex ampoule 0.8 cm i.d., 15.2 cm long at 217.8° for 220 min. The recovered (−)-*trans*-IV had $[\alpha]^{28}_D$ $-130.6°$ (86.2% retention of optical activity). The amount of *cis*-IV formed was 9.9%.

(b) **Thermal Isomerization of (+)-*cis*-IV.** (i) **At 1 mm Pressure.** (+)-*cis*-IV (50 mg), obtained by the base-catalyzed epimerization of (−)-*trans*-IV, $[\alpha]_D$ $-196°$ (96.3% optical purity), was vacuum transferred within 5 min into the 12-l. flask (see above) and

heated for 150 min at 217.5°. The product was recovered almost quantitatively. It was analyzed and separated as described earlier. The optical purity of the recovered *cis*-IV was determined as usual *via* *trans*-IV, $[\alpha]_D$ $-161.8°$ (82.5% retention of optical activity). The product *trans*-IV had $[\alpha]_D$ $-63.7°$.

(ii) **In Benzene.** A solution of (+)-*cis*-IV (30 mg) of 96.3% optical purity, in 0.5 ml of dry benzene, was heated in a thick-walled sealed Pyrex ampoule 0.8 cm i.d., 15.2 cm long for 150 min at 217.8°. The optical activity of the recovered *cis*-IV was determined through its conversion to *trans*-IV, $[\alpha]_D$ $-175°$ (89.3% retention of optical activity). The product *trans*-IV had $[\alpha]_D$ $-62°$.

# 1,1'-Azobisformamide. I. Photochemical Decomposition in Solution[1]

Richard M. Fantazier* and John E. Herweh

Contribution from the Armstrong Cork Company, Research and Development Center, Lancaster, Pennsylvania 17604. Received July 26, 1973

Abstract: The photolysis of 1,1'-azobisformamide (ABFA) has been investigated in DMSO solution ($\lambda > 300$ nm). The major photolysis products are N_2 (0.98–1.0 mol/mol of ABFA), CO (0.87–0.97) and urea (0.78). Ammonia and biuret are minor products (*ca.* 0.04–0.07). The photolysis is characterized by an induction period preceding the appearance of decomposition products. Spectrophotometric experiments indicate that the isomerization of ABFA is the only photochemical process occurring. Evidence is presented for a decomposition mechanism involving the cyclization of *cis*-ABFA to 1,2,4-triazoline-3,5-dione followed by thermal decomposition (25°) of the latter. The photolysis of N,N'-diethylazobisformamide under the same conditions yields primarily 4-ethylurazole while N,N,N',N'-tetramethylazobisformamide yields its cis isomer as the only photolysis product.

The thermal decomposition of α,α'-dicarbonyl azo compounds has not received a great deal of study, although their use as dienophiles[2] and as oxidants[3] has been investigated extensively. Published work on the thermal decomposition[4] suggests that free radicals are intermediates, analogous to the recognized behavior of aliphatic azo compounds. Photolysis, on the other hand, may involve several processes. For example, both photoisomerization[5] and homolytic pathways[4i] are important for azodicarboxylates. The mechanism of

photodecomposition of dimethyl azodicarboxylate has been considered only briefly, with the conclusion that free radicals are intermediates.[4a] Photolysis of dibenzoyldiimide[4e] and both *o,o'*- and *p,p'*-dichloro derivatives[6] yields predominantly benzils by a process that may involve isomerization to cis followed by simultaneous loss of nitrogen and formation of the carbon–carbon bond.[4f] Of all the α,α'-dicarbonyl azo compounds investigated, azobisformamides are among the least studied. Our primary interest is in the parent compound 1,1'-azobisformamide (ABFA). This com-

$$H_2NCON{=}NCONH_2$$
ABFA
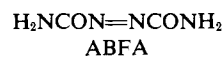
pound possesses considerable thermal stability. In the solid state it does not decompose significantly at temperatures below 190°. It is insoluble in most common solvents and possesses only limited solubility in dimethyl sulfoxide (DMSO), dimethylformamide (DMF), and similar solvents. Its decomposition mechanism in solution has never been reported. We have undertaken an investigation of its decomposition and are reporting herein the results of a study of its photolysis in solution.

(1) Presented in part at the 166th National Meeting of the American Chemical Society, Chicago, Ill., Aug 1973.

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(3) (a) F. Yoneda, K. Suzuki, and Y. Nitta, *J. Amer. Chem. Soc.*, **88**, 2328 (1966); (b) G. O. Schenck and H. Formaneck, *Angew. Chem.*, **70**, 505 (1958); (c) C. Cookson, I. R. Stevens, and C. T. Watt, *Chem. Commun.*, 259 (1965).

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Table I. Products from the Photolysis of ABFA, DEABFA, and TMABFA[a]

Compd	Solvent	Concn, M	N$_2$	CO	Urea	Biuret	Ammonia
ABFA	DMSO	0.16–0.21	0.98	0.87	0.78	0.07	0.053
	DMSO	0.34	1.00	0.97	0.78	0.04	Pres.[c]
	DMF[d]	0.17	0.88	0.79	0.58	0.13	

			N$_2$	CO	1	EtNH$_2$	
DEABFA	DMSO	0.34	0.20	0.005	0.46	Pres.[c]	
TMABFA	DMSO[e]	0.15	No decomposition occurs				
	DMF	0.04	Cis isomer, 0.22				

[a] Reactions at ambient temperature, photolysis with a 200-W mercury arc through Pyrex, to completion of gas evolution, usually 18–24 hr. [b] Product yields are the average of two or more experiments. [c] Present but not determined quantitatively. [d] Other products include biurea, 0.03, and N,N-dimethylurea, 0.02. This was a single experiment. [e] Photolysis for 42 hr.
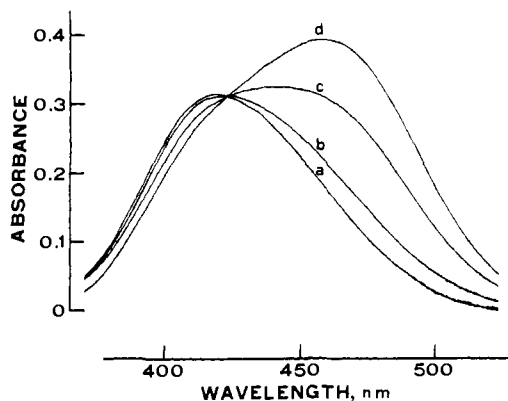

Figure 1. Differential absorption spectra for ABFA (0.043 M) in DMF at −35°, irradiate (150-W xenon lamp, Corning No. 7-51 filter) for periods of: (a) 0.0, (b) 1.0, (c) 2.0, and (d) 3.0 min. Reference is ABFA (0.036 M) in DMF.
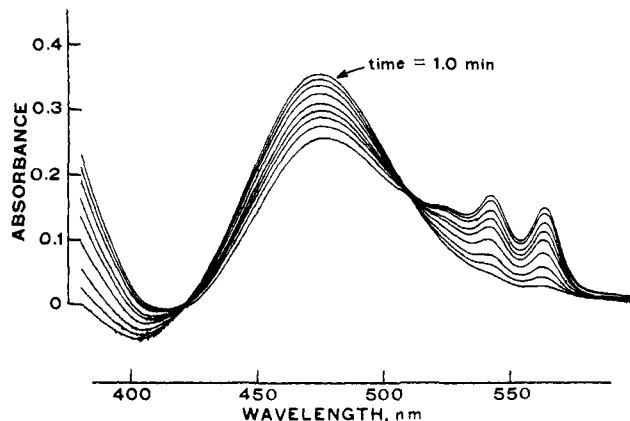

Figure 2. Differential absorption spectra of a mixture of cis- and trans-ABFA in DMF at 5°, recorded at times of 1.0, 3.0, 6.0, 11.0, 17.0, 22.0, 29.0, 36.0, and 46.0 min, respectively.

Results

1,1′-Azobisformamide. The photolysis of ABFA was conducted at ambient temperature in dry, nitrogen-purged DMSO and DMF solutions using a conventional immersion reactor with a 200-W mercury arc and Pyrex filter. The experiments were allowed to run until gas evolution had ceased. Clear, colorless solutions remained. Only three major photolysis products resulted: nitrogen, carbon monoxide, and urea. Other products were found in minor amounts. The material balance was typically very good with most of the starting ABFA accounted for. The decomposition products are shown in Table I.

In all cases, gas evolution did not begin immediately with ignition of the lamp but required several hours irradiation time until its commencement. Likewise, if the photolysis is interrupted after partial reaction, gas evolution persists for an hour or more. These results suggested that secondary, dark reactions play an important role in the photochemical decomposition process and prompted a study of the spectral changes occurring during the early stages of photolysis. These changes were followed by differential absorption spectrophotometry. A solution of ABFA in DMF (0.043 M) was irradiated at −35° within the spectrophotometer-cell compartment using a collimated beam of light from a 150-W xenon high-pressure lamp, filtered through a Corning 7-51 filter.[7] The absorption spectrum was

recorded after varying exposure times. A slightly more dilute ABFA solution (0.036 M) was used in the reference cell, which was not irradiated.[8] A set of differential curves for a typical experiment is shown in Figure 1. The most noteworthy features are the development of a new absorption band and the isosbestic at 423 nm. This new band is stable at −35°, but on warming to 5° disappears slowly with the formation of a new species having maxima at 545 and 565 nm. These spectral changes are shown in Figure 2. Two isosbestic points are present. After several hours at 5°, or upon warming to ambient temperature (24–26°), this last species disappears with the evolution of gas. At the completion of this decomposition sequence, the ultraviolet spectrum reveals only the ABFA band, reduced from its initial intensity.

The spectral changes observed were irreversible under the conditions imposed. The occurrence of isosbestic points argues strongly for the single reaction path

$$\text{ABFA} \xrightarrow[-35°]{h\nu} \text{A} \xrightarrow{5°} \text{B} \longrightarrow \text{decomposition products}$$
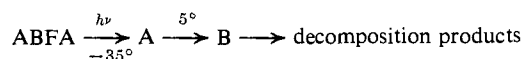
By this scheme, the maximum concentration of A produced at −35° equals the overall decrease in the concentration of ABFA observed. This makes possible a direct calculation of the extinction coefficient for A and also allows the absorption spectrum of A to be

(7) The Corning No. 7-51 filter has a transmission maximum at 365 nm (80%) which decreases to <1% at 310 and 415 nm.

(8) The use of a slightly more dilute reference solution was done as a matter of convenience to assure that the resulting differential curves maintained a conventional form with only positive absorbances.

Table II. Ultraviolet Absorption Data for ABFA and Related Compounds

Compound	Solvent	λ_{max}	ϵ_{max}
ABFA	DMSO	423	51.1
	DMF	419	58.3
cis-ABFA (intermediate A)	DMF ($-35°$)	469	180 ± 10
DEABFA	DMSO	434	51.8
	DMF	430	49.9
	Diglyme	429	46.6
cis-DEABFA	Diglyme	470	120 ± 5
TMABFA	DMSO	424	59.5
	DMF	426	54.6
	ODCB	438	48.4
cis-TMABFA	DMF	461	101 ± 5
2 (intermediate B)	DMF	525 (sh)	165
		542	254
		563	240
4	Diglyme	527	

Table III. Photolysis Data for ABFA, DEABFA, and TMABFA at 25° [a]

Compound	Concn, M	Solvent	Irradiation time, sec	Light[b] intensity × 10^{16}	ϕ_{isom}	ϕ_{dec}
ABFA	0.038	DMSO	1100	6.43	0.08	0.08
			2300		0.07	0.07
			4200		0.07	
DEABFA	0.039	DMSO	1000	6.43	c	0.07
			2750			0.07
		Diglyme	500	6.17	0.12	
			1500		0.11	0.10
TMABFA	0.039	DMF	1000	6.27	0.09	
			2000		0.08	d
			5150		0.06	

[a] Solutions were irradiated in 2.0-cm cells with an Osram 150-W high-pressure xenon arc. A Corning 7-51 filter was used. [b] Light intensity, in quanta/sec, was determined by potassium ferrioxalate actinometry: C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc., Ser. A*, **235**, 578 (1956). [c] Isomerization is not observed at 25°. The cis isomer is not stable in DMSO. [d] TMABFA is not decomposed under these conditions; only isomerization is observed.

determined by difference. The data for A can then be used to perform the same calculations for B.

Intermediate B does not form appreciably at temperatures below 0°, while at 25° the conversion of A to B occurs at a rate that is comparable to the rate of decomposition of B, so that only a small buildup of B is observed. Ultraviolet spectral data for ABFA, A, and B are included in Table II. Prolonged photolysis of ABFA in DMF at $-35°$ (300 nm $< \lambda < 400$ nm) results in an increase in the concentration of A, which approaches a limiting value of 5.5%. No other absorption bands appear in the 300–600-nm spectral region during these experiments.

The approach to a photostationary concentration without any other changes occurring suggests the presence of two interconverting species, consistent with the isosbestic points observed (Figure 1). The longer wavelength, higher extinction n–π^* maximum for A relative to ABFA (Table II) indicates that the CO—N=N—CO chromophore is probably still intact with only some perturbation and is consistent with the generally observed behavior of cis azo compounds. We, therefore, conclude that A is the cis isomer of ABFA. This is further supported by the structure of B discussed below.

The disappearance of cis-ABFA at 5 and 25° in DMF yields straight-line, first-order kinetic plots with half-lives of 120 and 5 min, respectively. The photolysis of ABFA in DMSO (25°) results in the formation of cis-ABFA at concentrations approaching 15% of the initial ABFA. Note that this value is considerably greater than the 5.5% photostationary concentration found in DMF at $-35°$ (*vide supra*). Photostationary conditions do not exist in these experiments, however, since cis-ABFA is itself decomposing to B. Photolysis to low conversion of ABFA to cis-ABFA in DMSO allows the calculation of the quantum yield for isomerization (ϕ_{isom}). Likewise, photolysis followed by prolonged standing in the dark and subsequent determination of the net decrease in ABFA content allows the calculation of the quantum yield for decomposition of ABFA (ϕ_{dec}). Within experimental error, these values are identical as shown in Table III. Note that longer photolysis times result in a slight decrease in the calculated quantum yields, attributed to photoisomerization of cis-ABFA to trans.

Attempts to sensitize the decomposition of ABFA

in DMSO were not successful. Benzophenone and phenanthrene were used as sensitizers, at concentrations sufficient to absorb essentially all of the incident radiation below 380 nm that would otherwise be absorbed by the ABFA. Only the long wavelength absorption band of ABFA at 423 nm (DMSO) was irradiated directly in these experiments. Under conditions in which ABFA decomposition by direct photolysis is complete, these sensitized photolyses resulted in no detectable decomposition. In like manner, photolysis with radiation filtered to exclude wavelengths shorter than 400 nm also resulted in no decomposition.

Attempts were made to trap cis-ABFA by conducting the photolyses in the presence of cyclopentadiene, taking advantage of the reported greater reactivity of cis-α,α'-dicarbonyl azo compounds as dienophiles.[9] Photolysis of ABFA (0.21 M) and cyclopentadiene (0.21 M) in DMSO, until the cessation of gas evolution, yielded nitrogen (0.38 mol/mol of ABFA) and carbon monoxide (0.24 mol/mol of ABFA) compared with essentially quantitative yield in the absence of cyclopentadiene. No Diels–Alder adduct was isolated from the nonvolatiles. In one cyclopentadiene trapping experiment, an equivalent amount of *p*-toluenesulfonic acid (monohydrate) was added as a scavenger for basic reaction products. In this case, photolysis yielded no nitrogen or carbon monoxide, but the original ABFA was reduced to 30% of its initial concentration. No Diels–Alder adduct could be isolated from the reaction mixture.

Substituted Azobisformamides. Both N,N'-diethylazobisformamide (DEABFA) and N,N,N',N'-tetramethylazobisformamide (TMABFA) were prepared and subjected to the same photolysis conditions used for

$$\text{EtNHCON} = \text{NCONHEt}$$
DEABFA

$$\text{Me}_2\text{NCON} = \text{NCONMe}_2$$
TMABFA

1
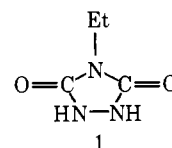
(9) B. T. Gillis and R. Weinkam, *J. Org. Chem.*, **32**, 3321 (1967).

ABFA. The photolysis products, included in Table I, reveal some significant differences. Although a complete material balance was not obtained for DEABFA, the results clearly indicate different reactions are occurring. Thus, the yield of nitrogen is greatly reduced, relative to that obtained from ABFA, and carbon monoxide is virtually eliminated as a product. The major, isolated product is 4-ethylurazole (1). Ethylamine was tentatively identified as a product but its yield was not determined. Spectrophotometric studies of DEABFA in DMSO or DMF at 25° revealed only the disappearance of the azo band during photolysis with no evidence for the formation of the cis isomer. The quantum yield of decomposition was about the same as found for ABFA (Table III). In diglyme as the solvent, photolysis of DEABFA at 25° results in the same behavior as observed for ABFA, namely the formation of a new absorption band (λ_{max} 470) with an isosbestic at 422 nm. This is assigned to the cis isomer of DEABFA (Table II). On standing this band disappears. These results indicate that cis-DEABFA is unstable in DMSO and DMF at 25° decomposing at a rate comparable to its formation. In diglyme, the reactions occurring parallel those found with ABFA. Isomerization appears to be the only photochemical reaction occurring. Quantum yield data (Table II) show a close agreement between isomerization and decomposition.

TMABFA was stable to photolysis. No decomposition occurs after irradiation for ca. twice as long as required to completely decompose ABFA (42 hr vs. 18–20 hr). Photolysis of a DMF solution of TMABFA showed only the formation of a new absorption band (λ_{max} 461) assigned to cis-TMABFA, with an isosbestic at 423 nm. Prolonged photolysis resulted in this band reaching a stationary level, calculated to be 21.9% cis. No further absorption bands were observed. Quantum yield data, shown in Table III, are the same order of magnitude as found for ABFA and DEABFA. This cis isomer of TMABFA was stable in DMF solution; its concentration was unchanged after standing in the dark for 24 hr at ambient temperature. No further photolysis experiments were conducted with TMABFA.

Discussion

The photolysis of aliphatic azo compounds generally results in decomposition with a loss of molecular nitrogen and the formation of a pair of free radicals.[10,11] The mechanistic details continue to be the subject of considerable research activity. In some cases, cis,trans isomerization is observed[12] and thermal decomposition of the cis isomer is an important pathway for hindered azo compounds.[13] With aromatic azo compounds, photolysis ($\lambda > 300$ nm) leads to cis,trans isomerization only, without decomposition.[14] Within the narrow limits of published work,[4a,e,5] α,α'-dicarbonyl azo

compounds do not appear to be efficient photochemical sources of free radicals, being closer in reactivity to diaryl azo compounds than to the azoalkanes. The photodecomposition of ABFA occurs by a process that does not fit a simple, free-radical mechanism. Homolytic decomposition with loss of nitrogen would yield a pair of formamoyl radicals (eq 1), half of which must

$$H_2NCON{=}NCONH_2 \longrightarrow 2H_2N\dot{C}O + N_2$$
$$H_2N\dot{C}O \xrightarrow[25°]{} H_2N\cdot + CO \qquad (1)$$
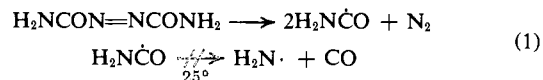
lose carbon monoxide to accommodate the quantitative yield of carbon monoxide. While precise data on the decarbonylation of the formamoyl radical are not available, fragmentary evidence from the literature indicates that this is not a favorable process at temperatures near 25°. Thus, the free-radical addition of formamide to various unsaturated substrates occurs in good yield both thermally and photochemically at temperatures up to 100°, without loss of carbon monoxide.[15,16] The decomposition of 2-cyano-2-propylazoformamide yields only traces of carbon monoxide at 100°.[17] Acyl radicals (R$\dot{C}$O) do not undergo decarbonylation readily below 100° unless the resulting radicals possess some degree of stability (e.g., t-Bu·, $C_6H_5CH_2\cdot$).[18] Thus, loss of carbon monoxide from the formamoyl radical to produce the energetic amino radical seems highly unlikely under our conditions. Moreover, formamoyl radicals add readily to ABFA.[15] Our products and material balance (Table I) are not consistent with any important contribution of such an addition reaction. Finally, the failure of the tetramethyl derivative (TMABFA) to undergo decomposition tends to discount any contribution of a free-radical pathway. If ABFA decomposes via homolysis, then TMABFA should reasonably decompose in the same way.

The presence of the two intermediates, A and B, formed sequentially, and producing a fairly simple set of products, argues for a simple decomposition mechanism for ABFA. The first step in the photolysis involves isomerization to cis-ABFA (intermediate A). Its conversion to B must not involve a great change in the cis-CON=NCO chromophore. Furthermore, B must be unstable at ambient temperature, decomposing quantitatively to nitrogen and carbon monoxide. These results are accommodated by the cyclization of cis-ABFA to 1,2,4-triazoline-3,5-dione (2), which exists as its ammonium salt (3) under the reaction conditions (eq 2). The ultraviolet spectrum of B is identical with that of 3, prepared by an alternate route, involving the oxidation of urazole with N_2O_4 followed by the addition of ammonia (eq 3). These results have been reported elsewhere by us.[19] The characteristic three-inflection absorption curve (Figure 2) for both 3 and B adds considerable support to the postulated identity of B. Furthermore, the cyclization reaction leading to B is substantiated by the formation of 4-ethylurazole (1) as a major product from the photolysis of DEABFA.

(10) (a) C. Walling, "Free Radicals in Solution," Wiley, New York, N. Y., 1957, p 544; (b) H. Zollinger, "Azo and Diazo Chemistry," Interscience, New York, N. Y., 1961, p 279.

(11) For recent references, see P. S. Engel and P. D. Bartlett, *J. Amer. Chem. Soc.*, **92**, 5883 (1970), and references therein.

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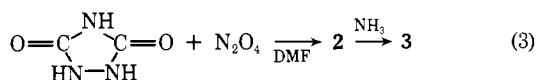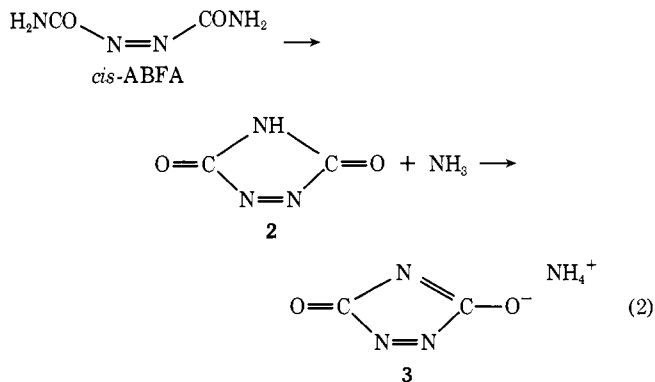(14) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966, p 465.

(15) R. M. Fantazier and J. E. Herweh, *J. Org. Chem.*, **38**, 2560 (1973).
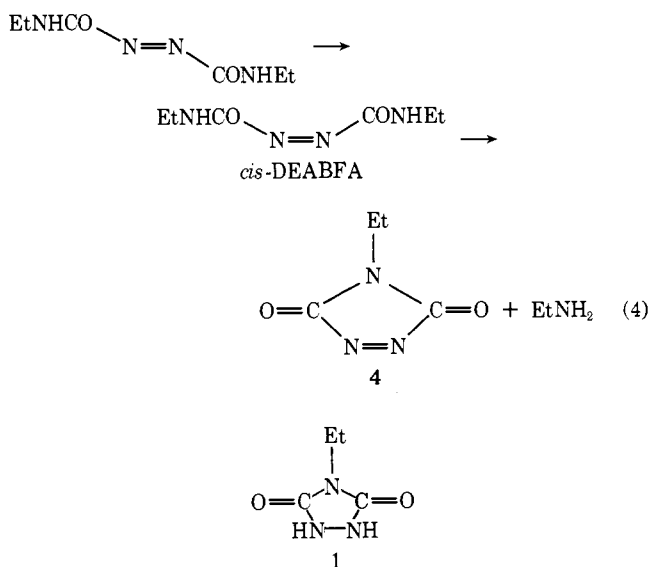
(16) H. H. Vogel, *Synthesis*, **3**, 99 (1970).

(17) J. C. Bevington and A. Wahid, *Polymer*, **4**, 129 (1963).

(18) C. Walling, "Free Radicals in Solution," Wiley, New York, N. Y., 1957, pp 277–279; M. G. Vinogradov and G. I. Nikishin, *Russ. Chem. Rev.*, **40**, 916 (1971).

(19) J. E. Herweh and R. M. Fantazier, *Tetrahedron Lett.*, 2101 (1973).

H₂NCO⟍N=N⟋CONH₂ →

cis-ABFA

$$O=C{\overset{NH}{\underset{N=N}{\Big\langle}}}C=O \ + \ NH_3 \ \longrightarrow$$

2

$$O=C{\overset{N}{\underset{N=N}{\Big\langle}}}C-O^- \quad NH_4^+ \quad (2)$$

3

$$O=C{\overset{NH}{\underset{HN-NH}{\Big\langle}}}C=O \ + \ N_2O_4 \xrightarrow[DMF]{} 2 \xrightarrow{NH_3} 3 \quad (3)$$

In the latter case, a reasonable mechanism leading to **1** involves cyclization of *cis*-DEABFA to the relatively stable 4-ethyl-1,2,4-triazoline-3,5-dione (**4**)[20] (eq 4).

EtNHCO⟍N=N⟍CONHEt →

EtNHCO⟍N=N⟋CONHEt →

cis-DEABFA

$$O=C{\overset{\overset{Et}{|}\!\!\overset{N}{}}{\underset{N=N}{\Big\langle}}}C=O \ + \ EtNH_2 \quad (4)$$

4

$$O=C{\overset{\overset{Et}{|}\!\!\overset{N}{}}{\underset{HN-NH}{\Big\langle}}}C=O$$

1

The urazole **1** most reasonably results from the reduction of **4** by ethylamine.[21]

Cyclization is not possible for TMABFA, and, in accord with the proposed mechanism, TMABFA does not decompose photochemically.

The products from the photolysis of ABFA must result from the decomposition of **3**, formed by the cyclization of *cis*-ABFA (eq 2). This decomposition is indicated by eq 5. The uv spectral data indicate that **3** is

$$O=C{\overset{N}{\underset{N=N}{\Big\langle}}}C-O^- \quad NH_4^+ \ \longrightarrow \ N_2 \ + \ CO \ + \ NH_4OCN \quad (5)$$
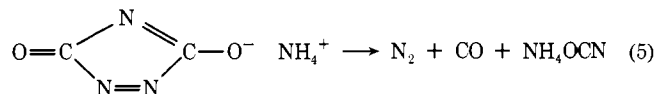
the major species formed, thus eq 2 and 5 probably best represent the decomposition pathway. Urea rather than ammonium cyanate is the major nonvolatile product. This result is reasonably attributed to the known, facile rearrangement of the cyanate.[22]

(20) A. V. Pocius and J. T. Yardley, *J. Amer. Chem. Soc.*, **95**, 721 (1973).
(21) C. M. Kraebel and S. M. Davis, *J. Org. Chem.*, **34**, 2226 (1969).
(22) (a) F. Wohler, *Am. Phys.*, **12**, 253 (1820); (b) *Ann. Chim. Phys.*, **37**, 330 (1828).

An alternate pathway which is indistinguishable from that described above involves the direct decomposition of **2** to nitrogen, carbon monoxide, and isocyanic acid (eq 6). Urea is then formed *via* the reaction of iso-

$$2 \longrightarrow N_2 + CO + HNCO \quad (6)$$

cyanic acid with ammonia (eq 7).

$$HNCO + HN_3 \longrightarrow H_2NCONH_2 \quad (7)$$

In addition to ammonia, biuret is a minor product, probably arising from the reaction of isocyanic acid with urea (eq 8).[23]

$$HNCO + H_2NCONH_2 \longrightarrow H_2NCONHCONH_2 \quad (8)$$
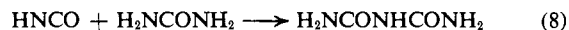
The decomposition of **2** (eq 6) is completely analogous to the reported pathway of *s*-triazolones and pyrazol-3-ones, generated *in situ* by oxidation of the corresponding *s*-triazolin-3-ones[24] and pyrazolin-*s*-ones[10] with lead tetraacetate. The decomposition of **2** and its salt **3** has been examined briefly under conditions resulting from oxidation of urazole with nitrogen tetroxide.[19] In the latter cases, hydrolysis reactions appear to be dominant. The major gaseous products are nitrogen and carbon dioxide.

The photolysis of ABFA in the presence of cyclopentadiene did not yield any isolable Diels–Alder adduct. However, the yield of nitrogen and carbon monoxide was substantially reduced. 1,2,4-Triazoline-3,5-dione (**2**) is a highly reactive dienophile,[19,25] while its salt **3** is not.[19] Since we have established **3** as the predominant, labile intermediate, we reasoned that Diels–Alder trapping would be enhanced by converting **3** to **2**. Therefore, an equivalent amount of *p*-toluenesulfonic acid was added to neutralize **3**. Photolysis with cyclopentadiene present under these conditions failed to yield volatile decomposition products, and no adduct could be isolated from the intractable product mixture. These experiments were not pursued further.

In a parallel study, we have examined the thermal decomposition of ABFA in DMSO solution in some detail over the temperature range 85–115°. The decomposition products (115°) are N₂ (0.88 mol/mol of ABFA), CO (0.38), biurea (0.13), biuret (0.23), urea (0.39), and cyanuric acid (0.008).[26] A complex decomposition mechanism is involved. A significant part of the decomposition is interpreted in terms of the mechanism developed above for the photolysis, but involving a *thermal isomerization* to *cis*-ABFA followed by cyclization to 1,2,4-triazoline-3,5-dione and its subsequent decomposition to N₂, CO, and urea. Carbon monoxide results from this pathway only. The remaining decomposition is accounted for by reaction involving free-radical intermediates and secondary reactions of products.

In support of a cyclization process, we find that DEABFA yields, at 115° in DMSO, predominantly a cyclic product, 4-ethylurazole, in 45% yield. Under the same conditions, TMABFA yields only nitrogen and products of free-radical decomposition. These results present a consistent picture for both the thermal

(23) For a discussion of the chemistry of isocyanic acid, urea, and biuret, see C. R. Noller, "Chemistry of Organic Compounds," 2nd ed, W. B. Saunders, Co., Philadelphia, Pa., 1957, pp 311–316.
(24) B. T. Gillis and J. G. Dain, *J. Org. Chem.*, **36**, 518 (1971).
(25) M. G. de Amezua, M. Lora-Tamayo, and J. L. Soto, *Tetrahedron Lett.*, 2407 (1970).
(26) J. E. Herweh and R. M. Fantazier, *J. Org. Chem.*, in press.

and photochemical decomposition of ABFA. Thermal decomposition clearly involves some isomerization, and possibly thermal isomerization is the predominant pathway in the thermolysis of ABFA and other azo compounds in general. These results will be published elsewhere.

Experimental Section

Ultraviolet spectra were recorded on a Beckman DK-2A spectrophotometer and infrared on a Perkin-Elmer Model 451 spectrophotometer. Nmr spectra (ca. 10% w/v) were recorded on a Jeolco Model JNM-4H-100 100-MHz spectrometer using internal TMS as a standard. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Melting points were determined in open capillary tubes on a Mel-Temp apparatus and are uncorrected.

Materials. 1,1'-Azobisformamide (ABFA) (Aldrich Chemical Co.) was used as received since analytical results were essentially unchanged from those of recrystallized material. Recrystallization from hot (80°) DMSO (20 g/200 ml) gave a 31% recovery of the azo compound: uv (DMSO) 423 nm (51.1); nmr (DMSO-d_6, 50°) δ 7.83 (s, broad); ir (KBr) 3350 (s), 3180 (vs), 1740 (vs), 1365 (s), 732 cm^{-1} (s). *Anal.* Calcd for $C_2H_4N_4O_2$: C, 20.69; H, 3.47; N, 48.27. Found for ABFA (as received): C, 20.80; H, 3.44; N, 48.41. Found for ABFA (recrystallized): C, 20.72; H, 3.29; N, 48.51. Functional group analysis (azo group) gave values of 59.1 and 59.7 for the equivalent weight of ABFA (as received) compared to a calculated value of 58.0. Urea (Fisher Scientific Co.) and biuret (Eastman Organic Chemicals) were dried *in vacuo* (P_2O_5) prior to use. Dimethyl sulfoxide (DMSO) and dimethylformamide (DMF), of reagent quality, were further purified by distillation from calcium hydride; fractions boiling at 73° (6.5 mm) and 151° (760 mm), respectively, were retained for use in this work.

N,N,N',N'-**Tetramethylazobisformamide (TMABFA).** A solid mixture of tetramethylhydrazobisformamide and triethylamine hydrochloride (10 g, containing 38.7% of the hydrazo compound, 22 mmol) suspended in 100 ml of methylene chloride was treated with a solution of lead tetraacetate [10.6 g (90%), 22 mmol] in 150 ml of methylene chloride.[27] The reaction temperature was maintained at 20 ± 2° by external cooling during the 15 min addition of lead tetraacetate.

Upon completing the addition and after stirring for 1 hr, the reaction mixture was added to cold water (200 ml). The methylene chloride and aqueous phases were separated; the former was washed consecutively with aqueous 10% sodium bicarbonate and saturated sodium chloride and dried over magnesium sulfate. Distillation of the dried methylene chloride solution (Rota-vap, hot water bath) left 2.9 g of crude tetramethylazobisformamide, mp 96–108°. One recrystallization of the crude azo compound (2.9 g) from a hexanebenzene combination (5:1) yielded 2.0 g of pure product: mp 111–113° (lit.[28] mp 112–113°): uv (DMSO) 424 nm (59.5); nmr (DMSO-d_6) δ 2.94 (2 s); ir (KBr) 2935 (w), 1715 (vs), 1400 (s), 1260 (s), 1145 (s), 788 (s) and 719 (m) cm^{-1}.

N,N'-**Diethylazobisformamide (DEABFA).** Reaction of ethylamine (1.2 mol) with diethylazodicarboxylate (0.6 mol) in dry benzene according to the procedure of Kraebel and Davis[21] gave DEABFA, mp 134–136° dec (38% yield). One recrystallization of crude DEABFA from THF gave material melting at 135–137° dec (lit.[29] mp 133–135° dec) that was used in the photolysis studies. Compound DEABFA is an orange, crystalline solid: ir (KBr)

3275 (s, NH), 1710 (vs, C=O), 1525 (m), 1295 (m), 1253 (m), and 1145 (m) cm^{-1}; nmr (DMSO-d_6) δ 1.13 (t, J = 6.25 Hz, 6 H), 3.30 (q, J = 6.25 Hz, 4 H), 8.8 (s broad, 2 H); uv (DMSO) 434 nm (54.7).

Photolysis of 1,1'-Azobisformamide. Photolyses were performed at ambient temperature in a Pyrex immersion reactor having a water-jacketed, quartz immersion well located in the center. The light source was a Hanovia 200-W medium-pressure mercury arc, situated within the quartz well. A Pyrex filter sleeve surrounded the lamp. The capacity of the reactor is approximately 400 ml. One side arm of the reactor was connected to a supply of high purity nitrogen for purging, the other side arm was connected to the gas train for separation and analysis of the volatile products. The gas train consisted of the following components, in order, ice trap, H_2SO_4 trap for ammonia, $Mg(ClO_4)_2$, Ascarite–$Mg(ClO_4)_2$ for CO_2, a combustion tube containing CuO maintained at 375° for oxidizing CO to CO_2, Ascarite–$Mg(ClO_4)_2$, and finally, a gas buret of 2500 ml capacity.

Typically, a solution of ABFA in dry, purified DMSO was prepared in a volumetric flask then transferred to the reactor. The reactor and gas train were purged with dry nitrogen for 5 min; then the lamp was ignited and nitrogen purging continued during a 5 min lamp warmup period. The nitrogen flow was stopped and the initial gas buret reading was taken. In all cases, gas evolution did not commence for several hours. The photolysis was stopped after all gas evolution had ceased (usually 20–25 hr after the start of photolyses). The yield of nitrogen was determined directly from the gas volume collected in the buret, corrected to standard conditions. The carbon monoxide yield was determined from the weight of CO_2 in the Ascarite tube following the CuO combustion furnace. Control experiments indicated 96–97% efficiency of the oxidation of CO to CO_2 by this method under typical reaction conditions. Ammonia was determined by titrating the contents of the H_2SO_4 trap. The photolyte was flash-distilled *in vacuo* (0.5 mm, <95°) to remove the solvent. The residue was triturated consecutively with benzene and ether. The nature of the dried solid residues was subsequently determined by nmr (DMSO-d_6) from a comparison with spectra of authentic samples. The amounts (per cent by weight) of the various components were calculated from the ratio of integrated areas of each component in relation to total integrated area (see Table I).

Photolysis of *N,N'*-Diethylazobisformamide. The general procedure described for the photolysis of ABFA was repeated using 23.07 g (0.134 mol) of DEABFA in 400 ml of DMSO (0.336 M). Upon termination of gas evolution (N_2, 0.027 mol and CO, 0.00007 mol), the rust to amber colored reaction mixture, possessing an amine-like odor, was flash distilled at 0.1 mm (pot temp <75°). The gummy, amber still residue was triturated with ether (4–100-ml portions) and then with boiling CHCl$_3$ (2–50-ml portions); 7.9 g of an ether and chloroform insoluble white solid remained, mp 194–196°. Recrystallization of the crude product (7.9 g) from diglyme gave analytically pure 1: mp 200–202° (lit.[30] mp 195–196°); ir (KBr) 3150 (m, broad), 1695 (s), 1485 (m), and 795 (w) cm^{-1}; nmr (DMSO-d_6) δ 1.10 (t, J = 7.0 Hz, 3 H), 3.38 (q, J = 7.0 Hz, 2 H), and 10.0 (s, broad, 2H). *Anal.* Calcd for $C_4H_7N_3O_2$ (1): C, 37.21; H, 5.46; N, 32.54; mol wt 129.1. Found: C, 37.26; H, 5.50; N, 32.61; mol wt, 130.0 (determined in DMF by vapor pressure osmometry).

Sensitized Photolyses. ABFA (10.0 g, 86.0 mmol) in 400 ml of DMSO containing benzophenone (33.6 g, 184 mmol) was photolyzed for 22 hr, during which time no gas was evolved. In another experiment, ABFA (9.75 g, 84 mmol) in 400 ml of DMSO containing phenanthrene (5.0 g, 28 mmol) was irradiated for 17 hr, during which time no gas evolution occurred. The ultraviolet absorption spectra were unchanged after photolysis.

(27) The tetrasubstituted hydrazobisformamide–triethylamine hydrochloride admixture was used directly as obtained from the reaction of dimethyl carbamoyl chloride (57 g, 0.53 mol) with hydrazine (8.4 g, 95%, 0.25 mol) and triethylamine (53.6 g, 0.53 mol) in chloroform (total volume 200 ml). No effort was made to effect separation of the hydrazo compound from the amine hydrochloride due to their ready solubility in water.

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