Some Novel Observations Concerning the Thermal Decomposition of 2,4,6-Trinitrotoluene

by Joseph C. Dacons, Horst G. Adolph, and Mortimer J. Kamlet

Advanced Chemistry Division, U. S. Naval Ordnance Laboratory, White Oak, Silver Spring, Maryland 20910

(Received January 22, 1970)

Samples of TNT were partially decomposed (*ca.* 10–25%) by heating for 16-hr periods at 200°. The complex decomposition product mixtures were shown by column chromatography to contain at least 25 discrete species as well as large amounts of a telomeric or polymeric material of indefinite composition ("explosive coke"). Sharply melting samples of seven of the decomposition products were isolated; three of these were identified as 4,6-dinitroanthranil, 2,4,6-trinitrobenzaldehyde, and 2,4,6-trinitrobenzyl alcohol. The absence in our decomposition residues of 1,3,5-trinitrobenzene, a decomposition product found by other workers, is demonstrated. Possible implications of these findings regarding reported activation parameters for TNT thermal decompositions are discussed.

Introduction

The thermal decomposition of 2,4,6-trinitrotoluene has been a subject of recurring interest for almost 50 years. Several investigators[1,2] have addressed themselves to the isolation and identification of intermediate products with a view toward elucidation of a stepwise decomposition mechanism; a more frequent approach[3-8] has involved the determination of apparent activation parameters for the overall process by comparison of time-to-explosion or gas evaluation data at a number of temperatures. Wide discrepancies between reported results of the latter types, determined over different temperature spans and under differing degrees of confinement (*e.g.*, activation energies ranging from 14 to 43.4 kcal/mol),[3-8] demonstrate that the process is far from well understood.

The significant and unresolved differences notwithstanding, however, differing sets of the reported activation parameters have recently been used as the bases for extended temperature range extrapolations to calculate reaction zone widths and induction times in the shock initiation of liquid TNT (estimated shock temperature *ca.* 880°).[9,10]

In the present paper we attempt to shed some light on the processes involved in the isothermal decomposition of TNT at 200°. Although the work reported here was carried out a number of years ago without the benefit of tlc, nmr, and other of the more recent analytical techniques, some of our results are of interest in that they differ significantly from the findings of other workers. They also demonstrate clearly the complexity and dependence of the thermal decomposition of TNT on reaction conditions and environmental factors as well as the pitfalls inherent in extended temperature range rate extrapolations.

Experimental Section

The mixtures of decomposition products used in the present study were obtained by heating TNT samples under air[11] as follows. In each of ten 9-in. Pyrex test tubes was placed 15 g of TNT (purified by several recrystallizations from acetone); the tubes were loosely fitted with glass stoppers to permit the escape of evolved gases and placed in a heating block which had been preheated to 200°. The block was of an insulated aluminum type, bored so as to accommodate each tube in its own compartment. The temperature was maintained at 200 ± 1° using a Brown potentiometer, Model 113CIPS-10, as a controller–recorder. The tops of the tubes protruded *ca.* 2.5 in. from the block, and small amounts of material which evaporated from the molten mass were condensed on the upper parts of the tubes or on the stoppers. At the end of the standard 16-hr period, the block was allowed to cool to 80° (4–5 hr required) and the samples were removed.

---

(1) R. N. Rogers, *Anal. Chem.*, **39**, 730 (1967).

(2) G. K. Adams, P. R. Rowland, and L. A. Wiseman, Ministry of Supply Report A. C. 3982, Great Britain, 1943.

(3) A. J. B. Robertson, *Trans. Faraday Soc.*, **44**, 977 (1948).

(4) J. Zinn and R. N. Rogers, *J. Phys. Chem.*, **66**, 2646 (1962).

(5) M. A. Cook and M. T. Abegg, *Ind. Eng. Chem.*, **48**, 1090 (1956).

(6) R. Robertson, *J. Chem. Soc.*, **119**, 1 (1921).

(7) T. Urbanski and S. Rychter, *C. R. Acad. Sci.*, **208**, 900 (1939).

(8) J. Wenograd, *Trans. Faraday Soc.*, **57**, 1612 (1961).

(9) J. W. Enig and F. J. Petrone, *Phys. Fluids*, **9**, 398 (1966).

(10) C. L. Mader, "A Study of the One-Dimensional Time-Dependent Reaction Zone of Nitromethane and Liquid TNT," Report LA-3297, Los Alamos Scientific Laboratory, Los Alamos, N. M., 1965; *Phys. Fluids*, **6**, 375 (1963).

(11) Control experiments where the decomposition was carried out under nitrogen did not show distinguishable differences from decompositions under air.

The combined decomposition residues from 150 g of TNT were digested in 1500 ml of boiling benzene for 30 min and filtered hot, and the insoluble material on the filter was washed with a further 1000 ml of boiling benzene. An insoluble residue consisting of varying amounts (almost nil to 18 g) of brown powdery material which did not melt at 360° was recovered (fraction C). This product ("explosive coke") burned with intumescence when ignited in a flame, leaving an abundance of carbon.

The filtrate, containing the soluble fraction, was concentrated under reduced pressure and used in subsequent chromatography.

Materials for Chromatography. All chromatographic tubes were of the tapered type. Chromatographic grade Silica (G. Frederic Smith Chemical Co., Columbus, Ohio) was ground in a ball mill for 5 hr and used without screening. Silicic acid was Mallinckrodt, Analytical Grade, 100-mesh powder. Celite 535 was obtained from Johns-Manville Products Co.

Preliminary Resolution of Benzene-Soluble Fractions. The soluble products from 250 g of TNT in 1250 ml of benzene were fractionated on five 70 × 270-mm columns of ground silica–Celite (5:1). Each column was prewet with benzene and a 250-ml aliquot of the solution was introduced. The column was then washed with 1600 ml of benzene, 1200 ml of benzene–methanol (9:1, v/v), 1500 ml of benzene–methanol (1:1, v/v), and finally 1000 ml of acetone. The effluents from each solvent were taken as separate fractions, corresponding fractions were combined, and the solids in each were recovered by evaporation under reduced pressure. Fractions 1–4 yielded 188, 17, 14, and 7 g of solids, respectively. The first fraction (fraction A) was nearly pure TNT, mp 78–81°. The chromatography of the intermediate fractions (combined, fraction B) is described in the next section. The final acetone fraction was combined with the benzene-insoluble material. Subsequent attempts to resolve the latter complex mixture of "explosive coke" components were not successful.

Chromatography of Intermediate Fractions. Fraction 2 from the preliminary separation was rechromatographed on eight 48 × 230-mm columns of silicic acid–Celite (5:1). Approximately 2.1-g quantities of the residue, dissolved in 30-ml portions of chloroform, were introduced on the columns after prewetting with 50 ml of *n*-hexane and developed with 900 ml of *n*-hexane–benzene (3:1). Although two zones were visible without streaking, the columns were extracted from the tubes and streaked with alcoholic sodium hydroxide to define the limits of the zones more clearly. The zones were cut from the columns; the corresponding zones were combined eluted with benzene–methanol (20:1) and, on evaporation of the solvent, yielded approximately equal quantities of solids. The amounts were not accurately determined. An additional 8.8 g of TNT was recovered from the combined effluents.

By rechromatographing zone 1, using a similar procedure, 2.5 g of 4,6-dinitroanthranil (**1**), mp and mmp 125–126° with authentic sample,[12] was recovered along with traces of TNT. Zone 2, on similar treatment, yielded 1.1 g of 2,4,6-trinitrobenzaldehyde (**2**), mp and mmp 118–119° with authentic sample,[13] and 200 mg of a compound, **6**, which on crystallization from benzene–*n*-hexane formed very fine tan needles, mp 225–227°. The identity of **6** has not been established, but the elemental analyses (Table I) indicate that it is a reduction product of TNT.

Fraction 3 from the preliminary separation was dissolved in 30 ml of dioxane and the solution was diluted with 130 ml of benzene. It was then chromatographed on two 70 × 270 mm columns of ground silica–Celite (5:1). Each column was prewet with 100 ml of benzene, 80 ml of the solution was introduced, and the column was developed with 2200 ml of benzene–methanol (200:1), 4800 ml of benzene–methanol (100:1), and 4000 ml of benzene–methanol (75:1). The resulting chromatograms showed two zones before and after streaking with alcoholic sodium hydroxide. The zones were cut from the columns and like zones were combined and eluted with acetone. On evaporation of the solvents, the recovery of materials was as follows: effluents, 2.1 g; zones 1, 3.6 g; zones 2, 7.0 g.

The effluent fraction was rechromatographed on silicic acid–Celite (5:1), using benzene–*n*-hexane solutions as developers. This resulted in the isolation of 1.4 g of **1**, 0.3 g of **2**, and 0.1 g of a compound, **5**, which formed white prisms, mp 132–133°, from benzene–hexane. The identity of **5** has not been established; analyses (Table I) indicate that it is an oxidation product of TNT.

Several attempts to isolate pure compounds from zone 1 were unsuccessful. It appeared to be a highly complex mixture. When zone 2 was rechromatographed on silicic acid–Celite (5:1), using benzene–hexane solutions as developers, 0.33 g of 2,4,6-trinitrobenzyl alcohol (**4**), mp and mmp 102–103° with authentic sample,[14] and 0.32 g of a compound, **7**, mp 221–222°, were isolated. The latter crystallized as straw-colored needles from benzene–hexane; analyses (Table I) indicate that it is a reduction product of TNT.

When the original benzene-soluble fraction was chromatographed on ground silica–Celite, using 800 ml of benzene–ethanol (100:1) as developer, two zones appeared near the bottom of the chromatogram. On rechromatographing the effluent from this trial on the same adsorbent, using 1500 ml of benzene–methanol, a complex chromatogram showing 11 poorly defined zones was produced. Extensive efforts to isolate pure products from these zones resulted in the recovery of

---

(12) J. S. Splitter and M. Calvin, *J. Org. Chem.*, **20**, 1086 (1955).

(13) "Beilsteins Handbuch," Vol. VII, p 265.

(14) "Beilsteins Handbuch," Vol. VI, 1st Suppl., p 224.

1, **2**, and a compound, **3**, mp 217–218°, which the analyses (Table I) indicated to be a reduction product of TNT. Attempts to obtain pure materials from the zones in the initial chromatogram were not successful; the use of silica–Celite columns was therefore discontinued.

Results and Discussion

As standard reaction conditions for the decomposition of TNT, a reaction temperature of 200° and a 16-hr reaction time appeared most appropriate. At lower temperatures, the reaction was too slow; samples heated to 150 and 180° for 70-hr periods, for example, showed only slight decomposition as indicated by melting point depressions of 1 and 3°, respectively, with only minor darkening of the resolidified mass in the latter instance.

At 200° intense darkening of the melt indicated a more rapid reaction. If not intercepted, this went over to an autocatalytic process which generally resulted in autoignition in about 37–39 hr. At 210° the spontaneous self-ignition stage was usually reached in 14–16 hr, but occasionally in appreciably shorter periods.

The process seemed highly susceptible to minor variations in procedure and to adventitious catalysis. The amount of TNT consumed in the decompositions varied from 10 to 25% and the relative proportions of the primary decomposition products varied over a two- to threefold range from run to run (*vide infra*). Further, for no known reason, several samples reached the self-burning stage before the standard 16-hr reaction period had been completed (*i.e.*, more than twice as rapidly as the norm).

Initial small-scale separations resulted in three main fractions: (A) 75–90% of unreacted TNT; (B) benzene-soluble decomposition products, probably of intermediate molecular weights (*i.e.*, 200–500) in amounts representing 5–10% of the starting TNT; (C) benzene-insoluble decomposition products, probably telomeric or polymeric (*i.e.*, molecular weights >500) in amounts ranging from essentially nil to 13 wt % of starting material (or 60% of consumed TNT). Taken with the fact that total weight losses attributable to evolved gases amounted to no more than several per cent when as much as 25% of the starting TNT had been consumed, the relative quantities and gross properties of these fractions, particularly fraction C, gave strong preliminary insights into the nature of the TNT thermal decomposition process.

Fraction C, a brown intractable powder ("explosive coke"), which did not melt below 300° and burned with intumescence when ignited by a flame leaving an abundance of soot, showed strong characteristic absorption near 1600 cm^{-1} in the infrared spectrum, indicating that it contained unreacted aromatic nitro groups and hence was still a reasonably energetic material. In appearance and properties it closely resembled a toluene-insoluble fraction described by Adams, Rowland, and Wiseman,[2] who reported that their material was reasonably soluble in molten TNT, acted as a strong decomposition catalyst, and showed an elemental analysis corresponding roughly to the empirical formula $C_6H_3N_2O_{3.75}$.

Implications Regarding Kinetic Studies and Activation Parameters. These and findings to be published subsequently from this laboratory point up a major difference between thermal decompositions of polynitro-, nitroxy- and nitroazaaliphatic and -alicyclic explosives, on the one hand, and polynitroaromatic explosives on the other. Compounds of the former types, *e.g.*, HMX (1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane),[15] generally decompose directly to relatively low molecular weight species, primarily gaseous, with little intermediate buildup of decomposition products in the condensed phase. For explosives of these types, determinations of evolved gases in thermal decompositions may represent fair measures of extents of reaction; we have no basis to question published kinetics by the gas evolution method in such cases.

In marked contrast with the above, however, TNT and a large number of polynitroaromatic compounds[16,17] generate relatively small amounts of gaseous products during their early decomposition stages[17] but instead go over to intermediate molecular weight decomposition products which self-condense to "explosive cokes" prior to ignition or detonation. Hoffsommer[17] has also demonstrated that, for most materials which go over to "explosive cokes," ratios of moles of gas evolved to moles of starting explosive consumed may vary over a five- to tenfold range depending on the extent of decomposition and the reaction temperature.

Hence, activation parameters for thermal decompositions of polynitroaromatic compounds, determined in the 200–420° range,[3-6] seem to us to be subject to serious question. Data deriving from time-to-explosion studies are suspect on the basis that the phenomena leading to explosion are likely to be governed by the properties and reactivity of the "explosive coke" rather than by primary processes involving the TNT. Data from gas evolution studies are equally uncertain inasmuch as they are likely to reflect strong inaccuracies arising from differing ratios of gas evolved to explosive consumed at different temperatures.

We therefore suggest that the use of such Arrhenius-type parameters for the mathematical treatment of

---

(15) B. Suryanarayana, R. J. Graybush, and J. Autera, *Chem. Ind. (London)*, 2177 (1967); "Proceedings of the 36th International Congress on Industrial Chemistry, Brussels, 1967," Vol. III, 1967, p 647.

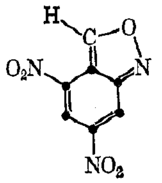
(16) Including *sym*-trinitrobenzene, picramide, 2,2′,4,4′,6,6′-hexanitrobiphenyl and its 3-amino and 3,3′-diamino derivatives, 1,3-diamino-2,4,6-trinitrobenzene, 2,2′,4,4′,6,6′-hexanitroazobenzene, and 2,2′,2″,4,4′,4″,6,6′,6″-nonanitro-*m*-terphenyl.[17]

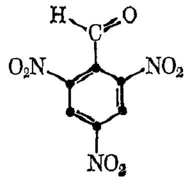
(17) J. C. Hoffsommer, "Thermal Stability of Polynitroaromatic Amines," Report NOLTR 65-227, U. S. Naval Ordnance Laboratory, Silver Spring, Md., Feb 16, 1966.

shock initiation phenomena at much higher temperatures[9,10] and for other extended temperature range extrapolations appears to be unwarranted. Further information regarding the strong dependence of the course and mechanism of TNT thermal decomposition on relatively minor changes in reaction conditions and temperatures, discussed in greater detail below, reinforces this view.

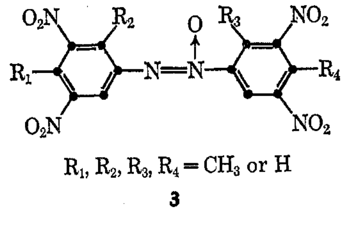
Isolation and Identification of Decomposition Products. Preliminary attempts to resolve fraction B by column chromatography showed that, even in its early stages, the TNT thermal decomposition was of a highly complex nature. Streaking the various columns with alcoholic alkali disclosed the existence of *more than 25 distinct zones,* each probably attributable to a unique monomeric (single aromatic nucleus) or dimeric (two aromatic nuclei joined) molecular species deriving from TNT. Two of these products were seen to be present in significant quantities; the others, in minor amounts only.

Repeated rechromatographing of the benzene-soluble fraction from 10 to 15 combined 15-g decomposition batches on silica-Celite, followed by fractional crystallization, resulted in the isolation of sharply melting samples of the two major components of the mixture, together with one of the lesser products. The first of the major decomposition products, mp 125–126°, was identified as 4,6-dinitroanthranil (**1**) by comparison (infrared spectrum and mixture melting point) with an independently prepared authentic sample.[12] Elemental analyses of the second major component, mp 118–119°, corresponded well with calculated values for 2,4,6-trinitrobenzaldehyde (**2**); this identity was also confirmed by comparison with an authentic sample.[13] In these and the subsequent trials at separation (*vide infra*), the amounts of **1** accounted for between 7 and 20% of the consumed TNT and those of **2** for 4–10%.


1

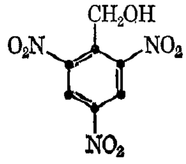

2

The minor component **3**, amber crystals, mp 217–218° dec, was isolated in only one instance and in milligram quantities. Elemental analyses, melting point, and solubility properties suggested that it was a dimeric reduction product of TNT, containing a bridging azo or azoxy linkage


$R_1, R_2, R_3, R_4 = CH_3$ or H

3

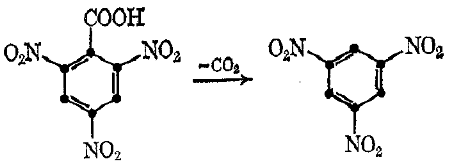
Subsequent chromatography on silicic acid–Celite led to the isolation of four additional minor decomposition products (but never again of **3**). No one of these additional products accounted for as much as 1% of the consumed TNT.


4

One of these compounds obtained from the further trials was readily characterized as 2,4,6-trinitrobenzyl alcohol (**4**), mp 102–103°, by comparison with an authentic sample.[14] Insufficient quantities of the other products were available for full characterization, but elemental analyses and solubility properties indicated that **5**, mp 132–134°, was also an oxidation product of TNT, and that **6** and **7**, mp 225–227 and 221–222°, respectively, were dimeric reduction products with structures analogous to **3**. The results of the various trials at separation and data serving toward product identification are summarized in Table I.

Nonappearance of Trinitrobenzene among Decomposition Products. Of at least as much interest as those decomposition products which we succeeded in isolating was one compound which failed to appear. Formally (but not necessarily in terms of mechanism), **4** and **2** are successive stepwise oxidation products of TNT. The logical sequential steps are to 2,4,6-trinitrobenzoic acid (**8**) and, since the latter compound is known to undergo ready decarboxylation at advanced temperatures, to 1,3,5-trinitrobenzene (TNB, **9**). TNB has been shown to be quite stable at temperatures as high as 280–300°.[17]

$$\text{TNT} \xrightarrow{[O]} \mathbf{4} \xrightarrow{[O]} \mathbf{2} \xrightarrow{[O]}$$


8 **9**

To ascertain where TNB would appear in our resolution schemes, mixtures of TNB with TNT and 4,6-dinitroanthranil (**1**) were chromatographed on silicic acid–Celite columns with benzene–*n*-hexane as developer. The TNB appeared as a discrete zone between TNT and **1**. Since, in our standard separations, **1** was the first of the decomposition products behind unreacted TNT, with a sizable interzone, TNB should have been easily detectable if present in our residues. Despite an exhaustive search, however, we were in no instance able to observe even traces of this material.

Our findings in these respects differ markedly from results by Rogers,[1] who recently described some pro-

Table I: Decomposition Products of TNT

Product	Recovery,[a] wt %	Mp, °C	Elemental analyses,[b,c] %		
			C	H	N
Unconsumed TNT	75–90	78–81	...	...	...
4,6-Dinitroanthranil (**1**)[d]	2–4	125–126	40.4	1.86	21.0
			40.0	1.75	20.8
			(40.2)	(1.43)	(20.1)
2,4,6-Trinitrobenzaldehyde (**2**)	1–2	118–119	35.1	1.42	17.6
			35.0	1.39	17.5
			(34.9)	(1.25)	(17.5)
Reduction product **3**[e]	<0.1	217–218 dec	42.1	3.11	23.2
2,4,6-Trinitrobenzyl alcohol (**4**)	~0.2	102–103	35.4	2.73	17.0
			34.5	2.69	17.2
			(34.6)	(2.06)	(17.3)
Oxidation product **5**	~0.04	132–134	35.3	1.09	16.4
			36.0	1.18	
Reduction product **6**[e]	~0.2	225–227	40.8	2.38	21.8
			41.0	2.68	22.1
Reduction product **7**[e]	~0.1	221–222	41.9	1.79	22.8
			41.6	2.44	22.7
"Explosive coke"	0–13	>360	...	...	...

[a] Based on starting TNT. [b] Elemental analyses of high-melting organic explosives are frequently poor because of the tendency of such compounds to decompose vigorously in the combustion tube. [c] Calculated values are in parentheses. [d] Molecular weight (X-ray) Found, 204. [e] *Anal.* Calcd for $C_{14}H_{10}N_6O_9$: C, 41.4; H, 2.47; N, 20.7.

grammed temperature pyrolyses of TNT (*ca.* 11° temperature rise/min from ambient temperatures to 300°), with separation and identification of products by thin layer chromatography. Rogers' reactions were conducted under a gas carrier stream; intermediate products were swept out prior to significant further reaction. No mention was made of polymeric material or "explosive coke" as a significant pyrolysis product.[1]

Whereas we isolated neither **8** nor TNB from our decompositions at 200° and definitely confirmed the absence of the latter, Rogers identified **8** as a minor product (which appeared at temperatures between 175 and 225°) and *TNB as the principal decomposition product* appearing between 233 and 285°. Further, our preliminary report[18] that **2** was a major product at 200° prompted Rogers to an intensive search for this species. Although he was able to identify trace amounts from the pyrolysis of some TNT-containing compositions, *2,4,6-trinitrobenzaldehyde never appeared under Rogers' conditions from pyrolysis of pure TNT.* In both Rogers' experiments and our own, **1** and **4** were observed in comparable amounts.

We can draw no firm conclusions from the differing findings regarding **8** since, from its position on Rogers' chromatograms, it may have been that minor amounts of 2,4,6-trinitrobenzoic acid were present in our decomposition residues but were lost with the "explosive coke" in our fraction C, nor is it conclusive from Rogers' description that small amounts of higher molecular weight materials (corresponding to **3**, **6**, and **7**, and our "explosive coke") were not also present in the tlc spot which he attributed solely to **8**.

The sharply contrasting findings regarding TNB and **2** do not seem subject to question, however, inasmuch as both species have been shown to be isolable and identifiable by both Rogers' techniques and our own. Here, the conflicting observations appear to signal an important change in TNT thermal decomposition pathways with changing reaction medium and/or changing time–temperature history over a relatively narrow temperature span.

A number of rationales may be advanced to account for this change in decomposition mechanism. (a) A sharp temperature threshold between our 200° and Rogers' 233° might arise from a very high activation energy in the TNB-forming reaction. This would require that the rate-determining step(s) in TNB formation differ markedly from that (those) in the TNT-consuming reactions. (b) Extraneous decomposition products, present in our mixtures but swept out of those of Rogers by his carrier gas stream, may react preferentially with **2** to form products other than TNB or otherwise inhibit the conversion of **2** to **8** and TNB. (c) TNB, although extremely thermally stable *per se*, may have undergone further rapid reactions with products present in our residues but swept out of those of Rogers. (d) Adventitious catalysis by a trace impurity, present in Rogers' TNT but absent in ours, may have led to rapid conversion of **2** to TNB. (e) The polymeric "explosive coke," present in significant amounts in our mixtures but not given time to form in

---

(18) J. C. Dacons, M. K. Kamlet, and D. V. Sickman, "Thermal Decomposition of TNT," Report NavOrd 6831, U. S. Naval Ordnance Laboratory, May 1, 1960.

those of Rogers, may have affected the course of the decomposition either by selective catalysis or through gross properties of the reaction medium.

Further observations which suggest that the properties of the medium and the nature of the coproducts play important roles by both increasing and decreasing reactivities of the various species are as follows. A 4-g sample of pure **2** was found to ignite spontaneously in less than 30 min at 200°; the amounts recovered from our residues require, however, that this aldehyde survives appreciably longer in the presence of its coproducts. On the other hand, **2** does seem to catalyze reactions of other species; 0.5 g of **2**, when admixed with 2 g of TNT, caused extensive decomposition of the latter after only 1 hr at 200°.

Any one of the phenomena mentioned above could markedly influence relative times-to-explosion or gas evolution rates. Taken in combination, they provide strong reinforcement to our views regarding the discrepancies and uncertainties in published activation parameters.

Acknowledgments. The authors are indebted to Dr. Darrell V. Sickman for useful discussions. The work was carried out under U. S. Naval Ordnance Laboratory Foundational Research Task FR-44.

Bonding in Dye Aggregates. Energetics of the Dimerization of Aqueous Cobalt(II)–4,4′,4″,4‴-Tetrasulfophthalocyanine Ion

by Z. A. Schelly, D. J. Harward, P. Hemmes, and E. M. Eyring

Department of Chemistry, University of Utah, Salt Lake City, Utah 84112 (Received April 3, 1970)

The thermodynamic functions $\Delta H°$, $\Delta G°$, and $\Delta S°$, as well as the activation parameters of the dimerization $2\text{M} \underset{{}_0k_{-1}}{\overset{{}_0k_1}{\rightleftarrows}} \text{D}$ of aqueous Co(II)–4,4′,4″,4‴-tetrasulfophthalocyanine ion (Co(II)–TSPC) were calculated using concentration–jump relaxation kinetic and equilibrium photometric data obtained at 38, 48, and 58°. The radius of the activated complex $r_{\ddagger}$ and the binding energy between the constituents in the dimer were calculated. The nature of binding forces and effect of the dielectric constant of the medium are discussed.

Introduction

In a recent paper[1] we reported on the kinetics of the dimerization of Co(II)–TSPC in aqueous solution at 58°. In the present work we focus on the energetics of this association equilibrium thus elucidating the reaction mechanism and the nature of binding forces between the constituents in the dimer.

This kinetic–thermodynamic approach should supplement the substantial spectroscopic–thermodynamic effort[2] which has been made to explain the forces in aggregates of charged or neutral dye molecules in general. The results show again the abilities of relaxation kinetic techniques to reveal intimate details of fast association processes.[3]

Based on the temperature dependence of the thermodynamic equilibrium constant K and the forward and reverse ionic strength independent rate constants ${}_0k_1$ and ${}_0k_{-1}$, respectively, we show below the results of a calculation of the standard molar reaction enthalpy $\Delta H°$, molar free energy change $\Delta G°_{331}$, and entropy of aggregation $\Delta S°_{331}$ of the reaction as well as the activation parameters

$$2\text{M} \underset{{}_0k_{-1}}{\overset{{}_0k_1}{\rightleftarrows}} \text{D}$$

$\Delta H_{\pm1}^{\ddagger}$, $\Delta G_{\pm1}^{\ddagger}$, and $\Delta S_{\pm1}^{\ddagger}$, for the forward (1) and reverse (−1) reactions, respectively. The important effect of the dielectric constant of the solvent on the rate constants and the nature of the bonding in the dimer are discussed.

Experimental Section

We have supplemented our previous concentration–jump relaxation kinetic and equilibrium photometric

---

[1] Z. A. Schelly, R. D. Farina, and E. M. Eyring, *J. Phys. Chem.*, **74**, 617 (1970).

[2] On the nature of bonding in dye aggregates, *cf.* K. K. Rohatgi and G. S. Singhal, *J. Phys. Chem.*, **70**, 1695 (1966), and references cited therein.

[3] M. Eigen and L. DeMaeyer in A. Weissberger's "Techniques of Organic Chemistry," Vol. VIII, Part II, Interscience Publishers, New York, N. Y., 1963, p 895 ff; E. F. Caldin, "Fast Reactions in Solution," Wiley, New York, N. Y., 1964.