This article was downloaded by:
On: *25 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Polymeric Schiff Bases. XI. Prototype Reactions of Some Monomeric Diarylidene Azines

G. F. D'alelio[a]; R. K. Schoenig[a]
[a] Department of Chemistry, University of Notre Dame, Notre Dame, Indiana

To cite this Article D'alelio, G. F. and Schoenig, R. K.(1968) 'Polymeric Schiff Bases. XI. Prototype Reactions of Some Monomeric Diarylidene Azines', Journal of Macromolecular Science, Part A, 2: 2, 367 — 405

To link to this Article: DOI: 10.1080/10601326808051418

URL: http://dx.doi.org/10.1080/10601326808051418

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

J. MACROMOL. SCI.—CHEM., A2(2), pp. 367-405, March, 1968

Polymeric Schiff Bases. XI. Prototype Reactions of Some Monomeric Diarylidene Azines*

G. F. D'ALELIO and R. K. SCHOENIG†

Department of Chemistry
University of Notre Dame
Notre Dame, Indiana

Downloaded At: 11:34 25 January 2011

Summary

The decomposition temperatures of 10 monomeric azines, $RC_6H_4CH{=}N{-}N{=}HCC_6H_4R$, are shown to be related qualitatively to the electronic nature of the R substituent, the contributing resonance structures, and hydrogen bonding, if present, in the azine moiety. The yields of nitrogen and stilbene are not quantitative and change with the nature of R. First-order kinetics are observed for the decompositions; deviations appear to result from side reactions. It is proposed that the decomposition is not exclusively through an ionic chain reaction but that it involves also a free-radical process and that the ratio of these two processes varies with R. The decompositions of certain substituted monomeric azines yield insoluble, infusible polymers.

The monomeric azines undergo the aldehyde, amine, and bis exchange reactions at below decomposition temperatures, similarly to the monomeric Schiff bases.

A study on the syntheses and properties of azine-type polymers, $\left[=HCArCH{=}N{-}N=\right]_n$, in which Ar represents an arylene moiety, was undertaken [1] as an extension of the work on polymeric Schiff bases which were shown [2–6] to have good thermal stabilities. Interest in the polymeric azines was stimulated by the fact that they may possess unusual ablative properties. The ablative properties are expected to arise from the fact that they suffer thermal decomposition, the

---

*This work has been supported by Grant NsG339 of the National Aeronautics and Space Administration, Washington, D.C.

†Taken in part from the Ph.D. Dissertation of R. K. Schoenig.

end product of which should be nitrogen and the thermally stable polystilbene:

$$\left[\!=\!HCArCH\!=\!N\!-\!N\!=\!\right]_n \xrightarrow{\Delta} N_2 + \left[\!=\!HCArCH\!=\!\right]_n \tag{1}$$

Curtius and Jay were the first investigators [7] to report the decomposition of azine monomers. From the products of decompositions, it was concluded that the major reaction was the following:

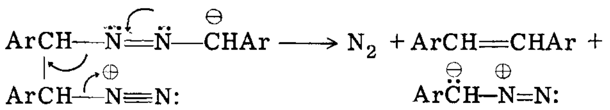
$$C_6H_5CH\!=\!N\!-\!N\!=\!HCC_6H_5 \longrightarrow N_2 + C_6H_5CH\!=\!CHC_6H_5 \tag{2}$$

The mechanism of this reaction remained dubious until recently.

In 1936 Williams and Lawrence investigated [8] the gas-phase decomposition of this azine. They concluded that the reaction was a first-order decomposition with $k_{607-608°K} = 0.15\ min^{-1}$ with an activation energy of $E_a = 53,000$ cal/mole. They also showed that under their experimental conditions, by-products, including benzonitrile, were obtained in addition to nitrogen and stilbene. The mechanism was reinvestigated [9] in 1960 by Zimmerman and Somasekhara [9], who reconsidered the kinetic data [8] of Williams and Lawrence, and proposed the following chain mechanism for the decomposition:

$$\text{Initiation:}\quad ArCH\!=\!N\!-\!N\!=\!HCAr \xrightarrow{k_i} Ar\overset{\ominus}{\ddot{C}}H\!-\!\overset{\oplus}{N}\!\equiv\!N\!: + ArCH\!: \tag{3}$$

$$\text{Propagation:}\quad ArCH\!=\!N\!-\!N\!=\!HCAr + Ar\overset{\ominus}{\ddot{C}}H\!-\!\overset{\oplus}{N}\!\equiv\!N\!: \xrightarrow{k_p}$$



(4)

$$\begin{array}{l} ArCH\!-\!\ddot{N}\!=\!\ddot{N}\!-\!\overset{\ominus}{C}HAr \\ | \\ ArCH\!-\!\overset{\oplus}{N}\!\equiv\!N\!: \end{array} \longrightarrow N_2 + ArCH\!=\!CHAr + Ar\overset{\ominus}{\ddot{C}}H\!-\!\overset{\oplus}{N}\!=\!N\!: \tag{4}$$

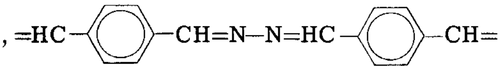
$$\text{Termination:}\quad Ar\overset{\ominus}{\ddot{C}}H\!-\!\overset{\oplus}{N}\!\equiv\!N\!: + X \xrightarrow{k_t} Y \tag{5}$$

In this sequence, the symbols X and Y represent unknown species in the termination process. The mechanism proposed is an ionic chain reaction involving an aryl diazomethane molecule, rather than a carbene, as the chain-carrying species. They also proposed [8] that this mechanism accounts for most of the phenomena and the products obtained in the decomposition of unsymmetrical azines, R–ArCH=N–N=HCAr, or from mixtures of ArCH=N–N=HCAr with RArCH=N–N=HCAr.

Before initiating studies on the syntheses and the properties of polymeric azines, we undertook prototype studies with various monomeric azines to confirm their decompositions to stilbenes and nitrogen and to obtain further information on the decomposition reac-

Downloaded At: 11:34 25 January 2011

Downloaded At: 11:34 25 January 2011

tions, the kinetics of the reactions, and the effects of substituents on the Ar moiety on the decomposition. Since the parent polymeric azine, poly-p-xylylidenehydrazine, $\left[HCC_6H_4CH{=}N{-}N \right]_n$, can be considered as having a segmer which is electronegatively substituted in the benzene ring, , several appropriately substituted monomeric azines, $R{-}C_6H_4CH{=}N{-}N{=}HCC_6H_4{-}R$, were synthesized to study their decomposition in reference to the unsubstituted parent axine, $C_6H_5CH{=}N{-}N{=}HCC_6H_5$.

In this study, the melting points of the monomeric azines were determined by differential thermal analyses and differ slightly from the melting points taken on a Fisher–Johns melting-point apparatus [10]. Differential thermal analytical methods were also used to characterize the decompositions of the monomers in nitrogen, as representative of an inert atmosphere, and in air, as typical of a reactive atmosphere.

Since in polymerization reactions involving these monomers, the use of Lewis acid catalysts is contemplated [1], the influence of p-toluenesulfonic acid and zinc chloride, respectively, on the decomposition of the monomers was also investigated.

The gas evolution method [8] was also used to characterize the monomers of this study, and the temperatures selected for the isothermal studies were arbitrarily chosen as midway between the temperature at which the onset of decomposition was observed as an endotherm in the thermogram and the maximum temperature observed at the completion of the endotherm. Also, since in some cases the polymers will be subjected to thermal environments which will increase from ambient or room temperatures to higher temperatures, the gas evolution method was used to evaluate the decomposition characteristics of the monomers as their temperatures were increased from room temperature to above their decomposition temperatures.

Since solution condensations of aryldialdehydes and hydrazine [1] were found to yield low molecular weight, insoluble brick-dust polymers, similar to those of polymeric Schiff bases when prepared by solution methods, it became also a purpose of this study to evaluate other syntheses of monomeric azines as prototypes for the syntheses of the polymers. The study of the prototype syntheses followed analogously those used for the Schiff bases, such as the carbonyl, amine, and bis exchange reactions [11], as well as reactions involving acetals [11, 12] as reactants. These reactions, which can be expressed as follows, were evaluated at temperatures below the previously determined decomposition temperatures of the reactants and derived azines:

The carbonyl exchange:

$$2X{-}C_6H_4CHO + C_6H_5CH{=}N{-}N{=}HCC_6H_5 \rightleftharpoons$$
$$2C_6H_5CHO{+}X{-}C_6H_4CH{=}N{-}N{=}HCC_6H_4X \qquad (6)$$

The amine exchange:

$$2C_6H_5CH{=}NC_6H_5 + H_2NNH_2 \rightleftharpoons$$
$$2C_6H_5NH_2 + C_6H_5CH{=}N{-}N{=}HCC_6H_5 \qquad (7)$$

The bis exchange:

$$2ClC_6H_4CH{=}NC_6H_5 + C_6H_5CH{=}N{-}N{=}HCC_6H_5 \rightleftharpoons$$
$$2C_6H_5CH{=}NC_6H_5 + ClC_6H_4CH{=}N{-}N{=}CHC_6H_4Cl \qquad (8)$$

The acetal reaction:

$$2C_6H_5CH(OC_2H_5)_2 + H_2NNH_2 \rightarrow$$
$$4C_6H_5OH + C_6H_5CH{=}N{-}N{=}HCC_6H_5 \qquad (9)$$

The acetal exchange:

$$2ClC_6H_4CH(OC_2H_5)_2 + C_6H_5CH{=}N{-}N{=}HCC_6H_5 \rightleftharpoons$$
$$2C_6H_5CH(OC_2H_5)_2 + ClC_6H_4CH{=}N{-}N{=}HCC_6H_4Cl \qquad (10)$$

Downloaded At: 11:34 25 January 2011

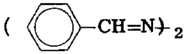
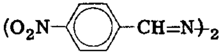
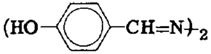
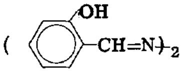
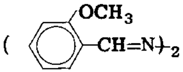
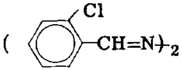
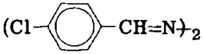
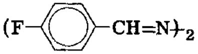
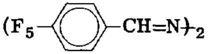
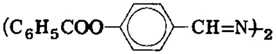
EXPERIMENTAL

Monomer Syntheses

The dibenzylidene azine, $C_6H_5CH{=}N{-}N{=}HCC_6H_5$, m.p. 93-94°C, lit. [13] 93°C, was prepared in a 96% yield by published procedures. Syntheses using the recently published [10] continuous azeotrope method were followed to prepare: di-(o-hydroxybenzylidene)-azine, m.p. [10] 219°C; di-(p-hydroxybenzylidene)-azine, m.p. [10] 287°C; di-(o-methoxybenzylidene)-azine, m.p. [10] 144°C; di-(pentafluorobenzylidene)-azine, m.p. [10] 137°C; and di-benzylidene-p-phenylenediamine, m.p. [10] 140°C. The same method [10] was used to prepare di-(p-chlorobenzylidene)-azine, m.p. 213°C, lit. [13] 213°C; di-(o-chlorobenzylidene)-azine, m.p. 143°C, lit. [13] 141°C; di-(p-nitrobenzylidene) azine, m.p. 306°C, lit. [13] 307°C; p-chlorobenzylidene aniline, m.p. 63°C, lit. [13] 63°C; and di-(p-fluorobenzylidene)-azine, m.p. 183°C.

Downloaded At: 11:34 25 January 2011

TABLE 1. Thermal Data on Some Monomeric Azomethines

	Azomethine	M.p., °C		Endotherm temp., °C						Decomposition residue
				In nitrogen			In air			
		N_2	Air	Onset	Mid-point	Maximum	Onset	Mid-point	Maximum	
I		94	94	306	317	328	302	320	338	Crystalline, soluble[a]
II		306	306	308	320	332	308	322	338	Polymer, insoluble[b]
III		285	285	285	295	305	285	294	303	Polymer, insoluble
IV		217	217	335	355	375	318	350	382	Polymer, insoluble
V		143	143	265	310	355	260	315	370	Crystalline, soluble
VI		144	144	292	310	328	285	310	335	Crystalline, soluble
VII		210	210	312	319	326	313	337	361	Crystalline, soluble
VIII		183	183	306	315	324	287	307	327	Crystalline, soluble
IX		137	137	262	285	308	237	265	293	Crystalline, soluble
X		228	228	275	335	395	275	338	399	Polymer, insoluble

[a] Soluble in acetone and common solvents.

[b] Insoluble in common solvents, dimethylacetamide, and concentrated (97.1%) sulfuric acid.

Downloaded At: 11:34 25 January 2011

Analysis: Calc'd. for

$C_{14}H_{10}N_2F_2$: C, 68.84; H, 4.13; N, 11.47; F, 15.59

Found : C, 69, 07; H, 4.43; N, 11.45; F, 15.72

The method [14] of Vörlander was used to synthesize $p\text{-}(C_6H_5COOC_6H_4CH{=}N)_2$, m.p. 228–229°C, lit. [14] 228°C. The syntheses of benzylidenediethyl ether and p-chlorobenzylidenediethyl ether have been reported previously [10, 11].

Melting and Decomposition Temperatures

A differential thermal method (DTA) was used to determine the melting and decomposition temperatures of the monomeric azines of this study. The apparatus used was the du Pont 900350 calorimetric cell in conjunction with the du Pont 900 thermoanalyzer. The sample weight was approximately 10 mg; the heating rate was 25°C/min. Deoxygenated nitrogen and air were used as sample atmospheres at a flow rate of 1 ft^3/hr. The melting and onset decomposition temperatures in nitrogen and in air are given in Table 1. Also tabulated are the midpoint temperatures observed between the temperatures of the beginning of the endotherms and that at the completion of the endotherms.

Typical decomposition thermograms in nitrogen for the monomeric azines are illustrated by Fig. 1 for dibenzylidene azine, Fig. 2 for di-(p-nitrobenzylidene)-azine, Fig. 3 for di-(p-hydroxybenzylidene)-azine, and Fig. 4 for di-(p-fluorobenzylidene)-azine.

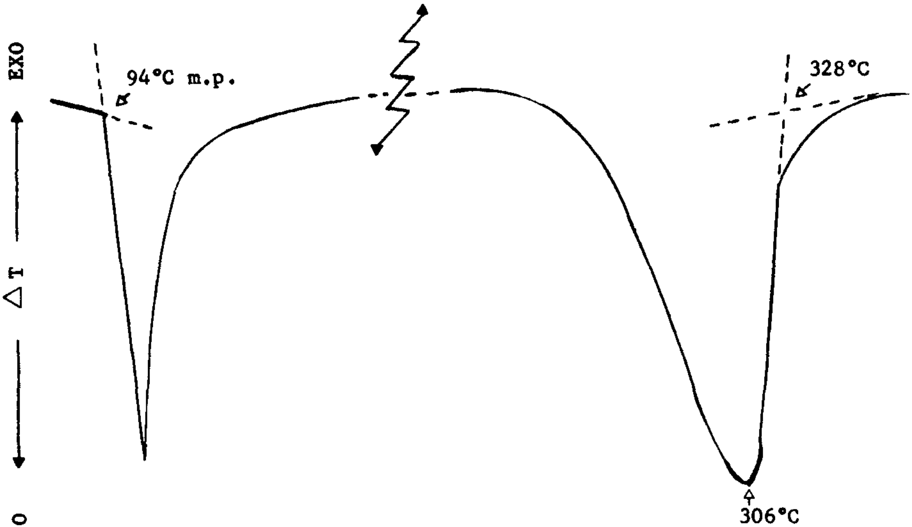
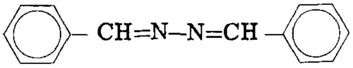


FIG. 1. Thermogram of  in nitrogen.

Downloaded At: 11:34 25 January 2011

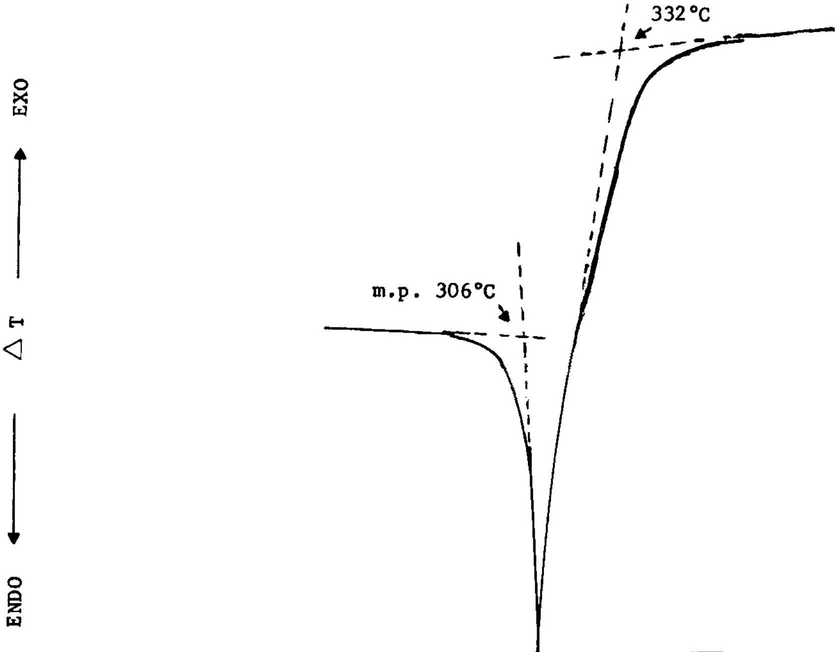
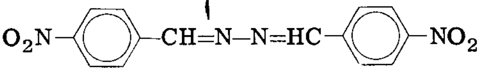


FIG. 2. Thermogram of  in nitrogen.

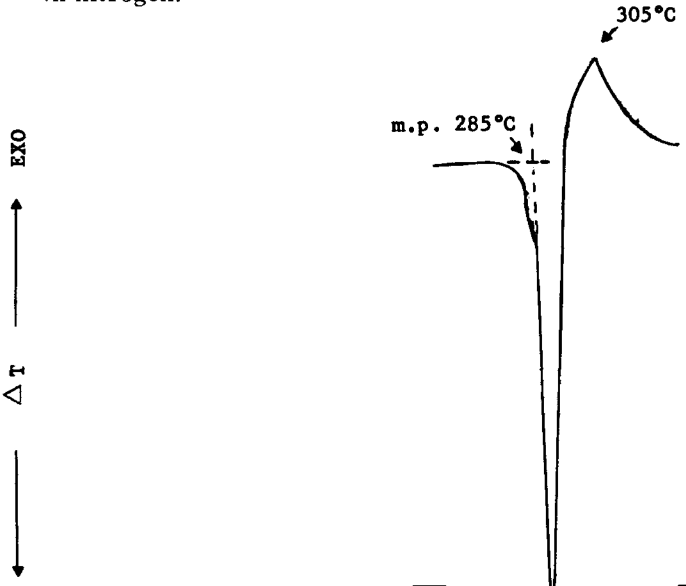
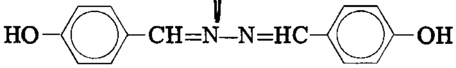


FIG. 3. Thermogram of  in nitrogen.

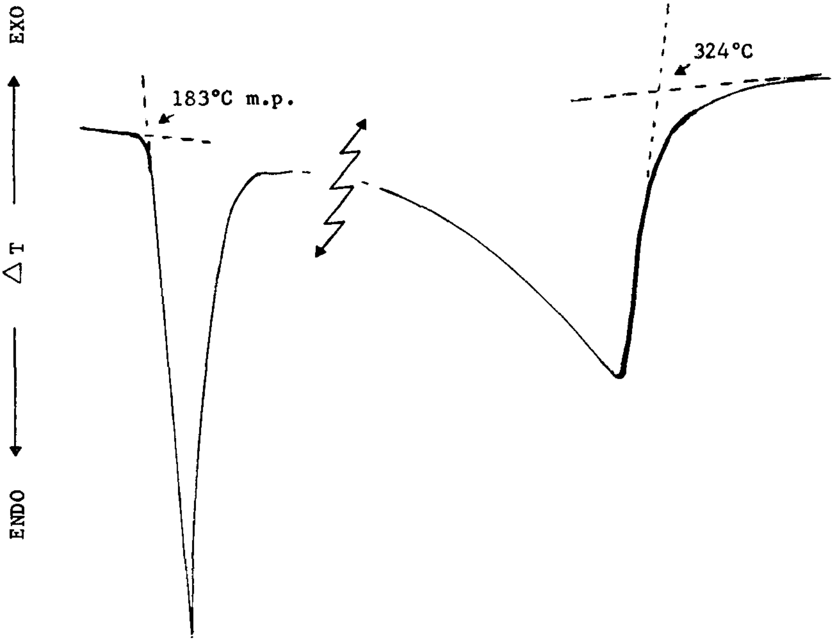
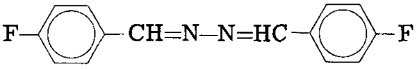


FIG. 4. Thermogram of  in nitrogen.

The infrared spectra of monomers II, III, IV, and X are given, respectively, in Figs. 5-8. The thermal decomposition of these monomers yielded infusible polymeric products. Finely ground samples of the crude polymeric products obtained from the decomposition of these monomers were extracted for 24 hr in a Sohxlet apparatus with ethanol, then dried at 100°C for 24 hr. The infrared spectra of the extraction-purified polymeric residues are given in Figs. 9 to 12. The infrared spectra of the extracted samples were substantially similar to those of the unextracted samples except for II and X, in which cases the extracted product showed the absence of bands characteristic for NO_2 in II, and C_6H_5CO in X, which were originally present in the crude reaction product either as unconverted monomer or as nonpolymeric by-product. Each of the four unextracted and extracted polymeric residues were subjected to thermogravimetric analysis at a heating rate of 10°C/min in a nitrogen atmosphere at a gas flow rate of 1 standard liter/min. The thermograms for the polymeric residues from II, III, IV, and X are given in Figs. 13 to 16.

Downloaded At: 11:34 25 January 2011

Downloaded At: 11:34 25 January 2011

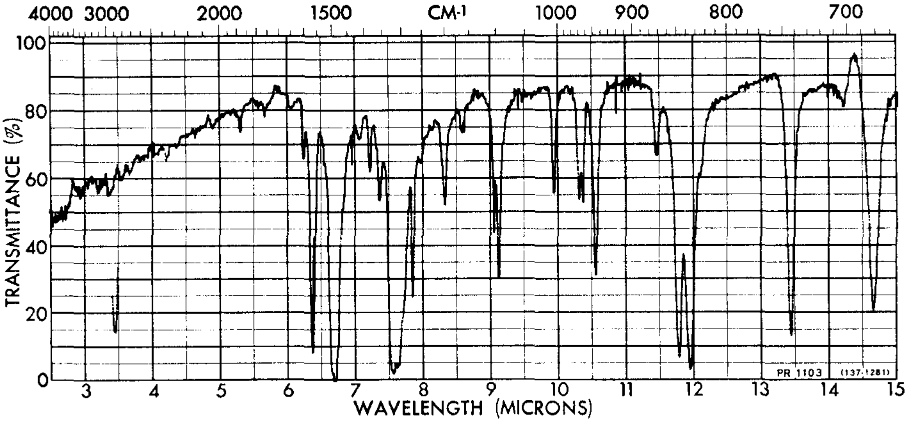
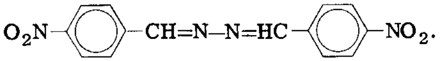


FIG. 5. Infrared spectrum of



. KBr disc.

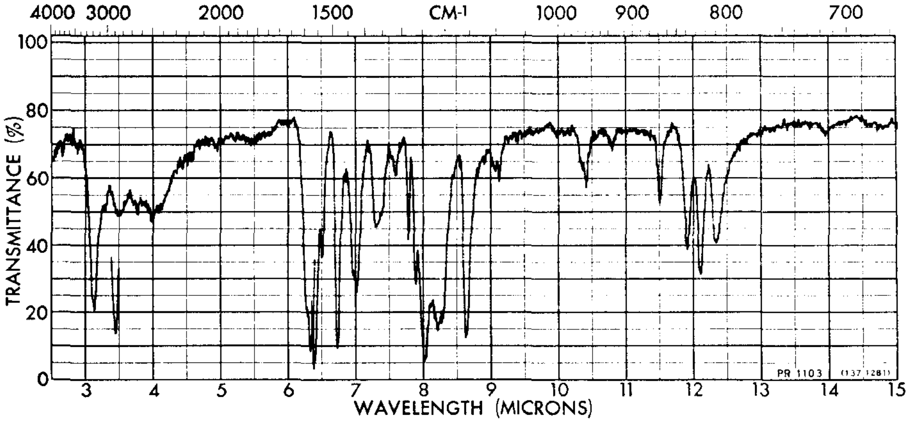
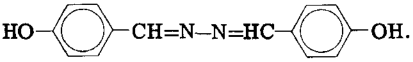


FIG. 6. Infrared spectrum of



. KBr disc.

Downloaded At: 11:34 25 January 2011

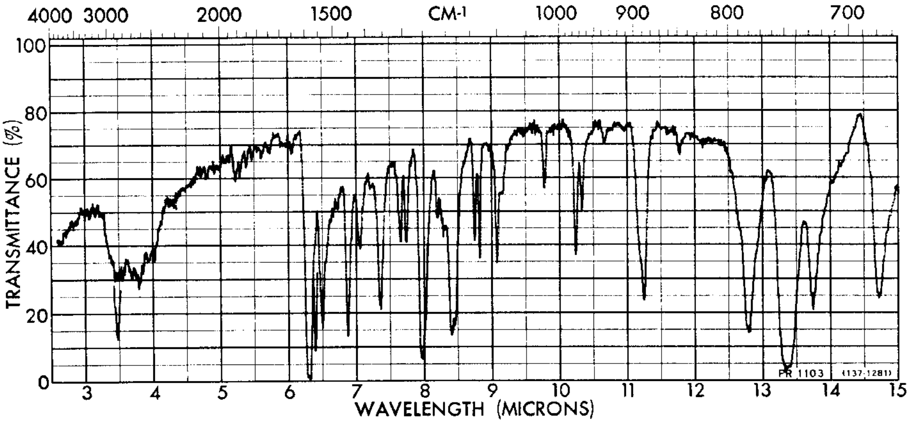
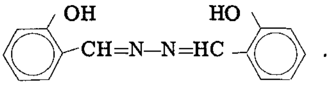


FIG. 7. Infrared spectrum of 

. KBr disc.

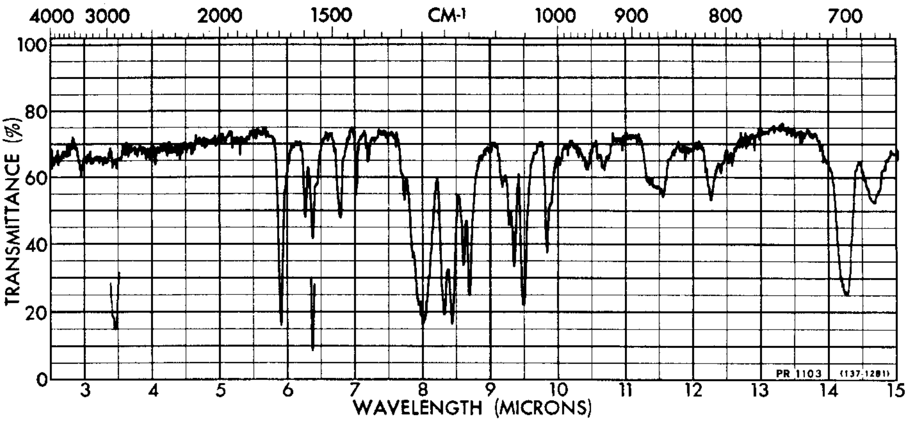
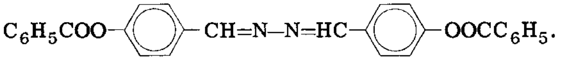


FIG. 8. Infrared spectrum of



. KBr disc.

Downloaded At: 11:34 25 January 2011

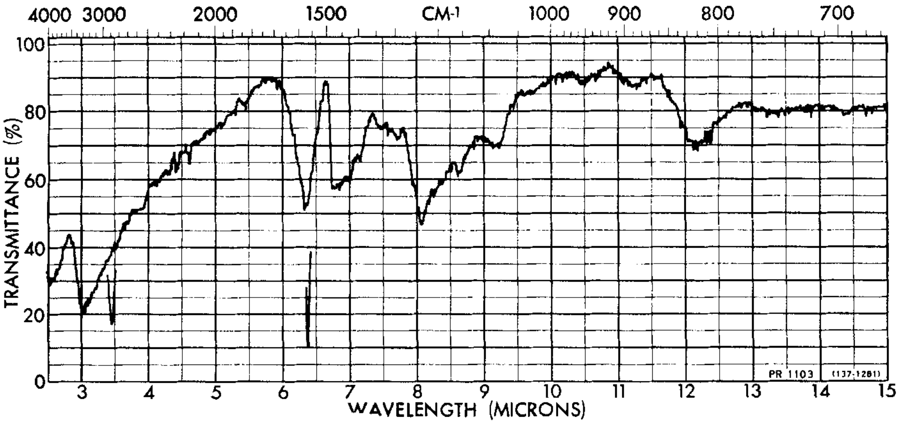
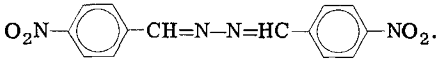


FIG. 9. Infrared spectrum of polymeric residue obtained from the decomposition of  KBr disc.

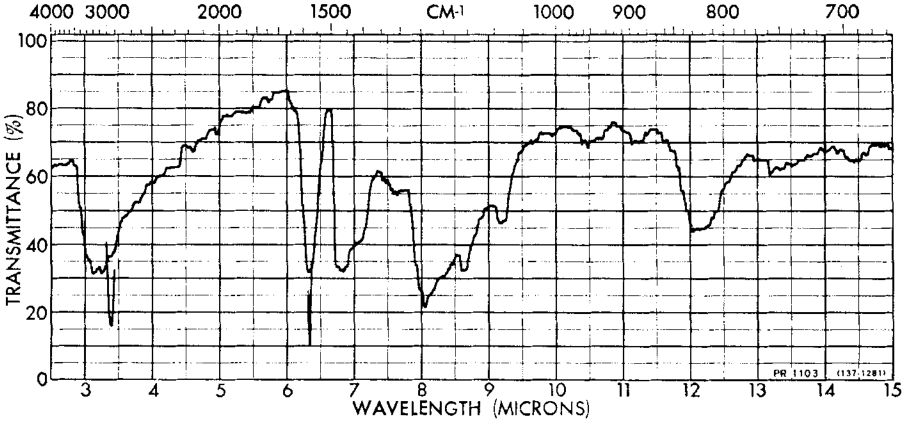
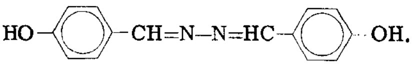


FIG. 10. Infrared spectrum of polymeric residue obtained from decomposition of  KBr disc.

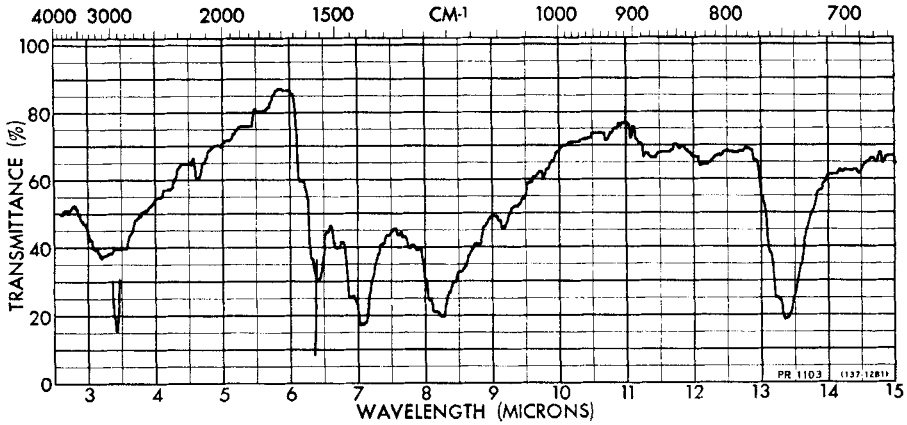
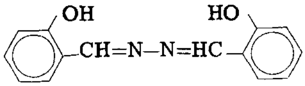


FIG. 11. Infrared spectrum of polymeric residue obtained from decomposition of  $o\text{-}HOC_6H_4CH{=}N{-}N{=}HCC_6H_4OH\text{-}o$ KBr disc.

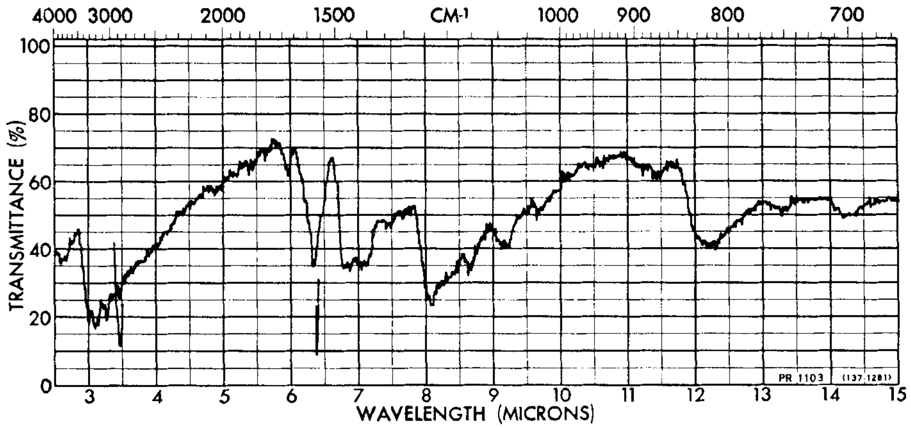
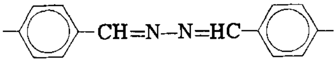


FIG. 12. Infrared spectrum of polymeric residue obtained from heating C_6H_5COO$OOCC_6H_5$. KBr disc.

Downloaded At: 11:34 25 January 2011

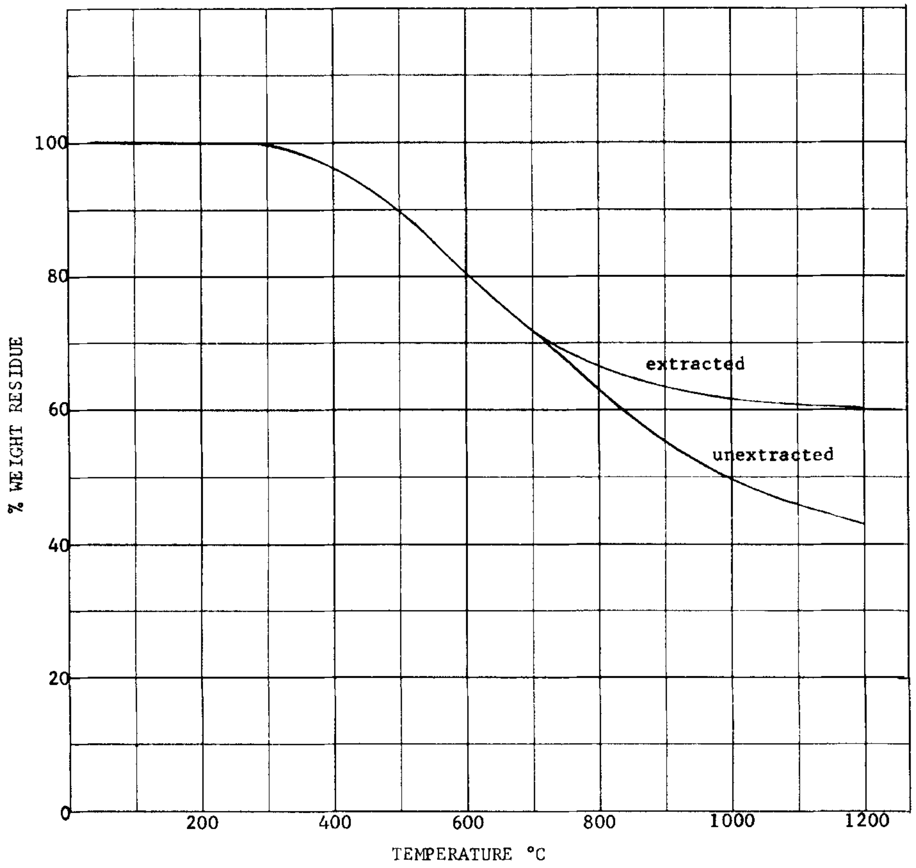
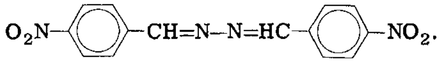


FIG. 13. Thermogram in nitrogen of polymeric residue obtained from decomposition of .

Downloaded At: 11:34 25 January 2011

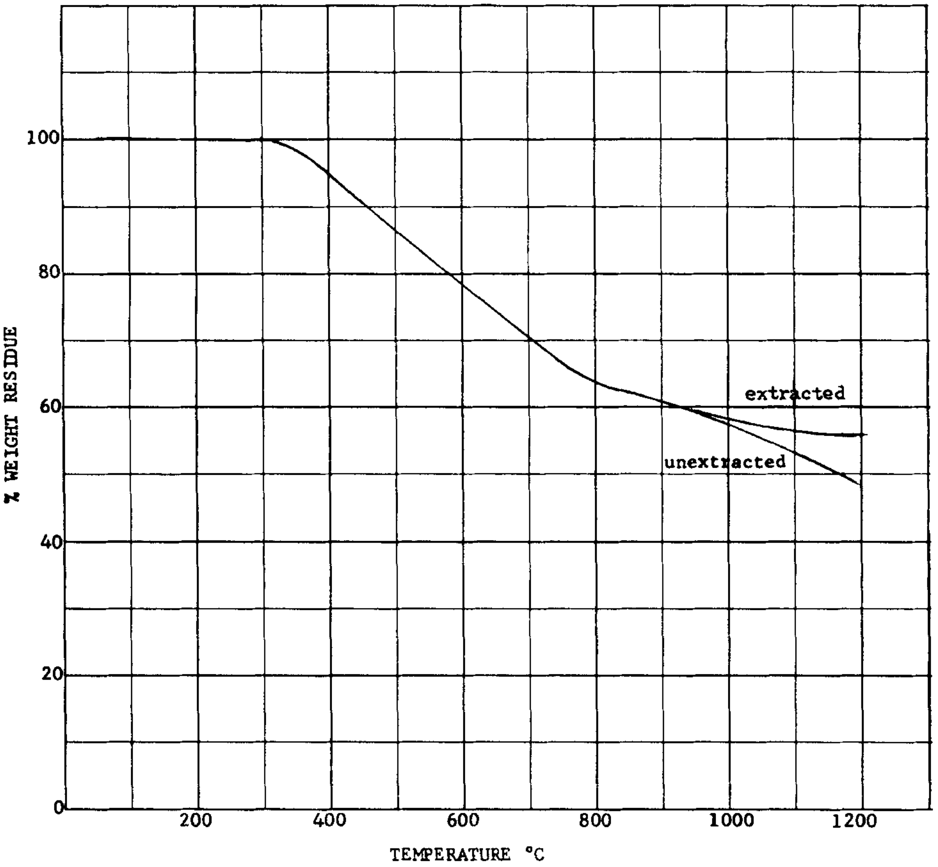
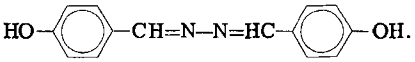


FIG. 14. Thermogram in nitrogen of polymeric residue obtained from decomposition of



Downloaded At: 11:34 25 January 2011

Downloaded At: 11:34 25 January 2011

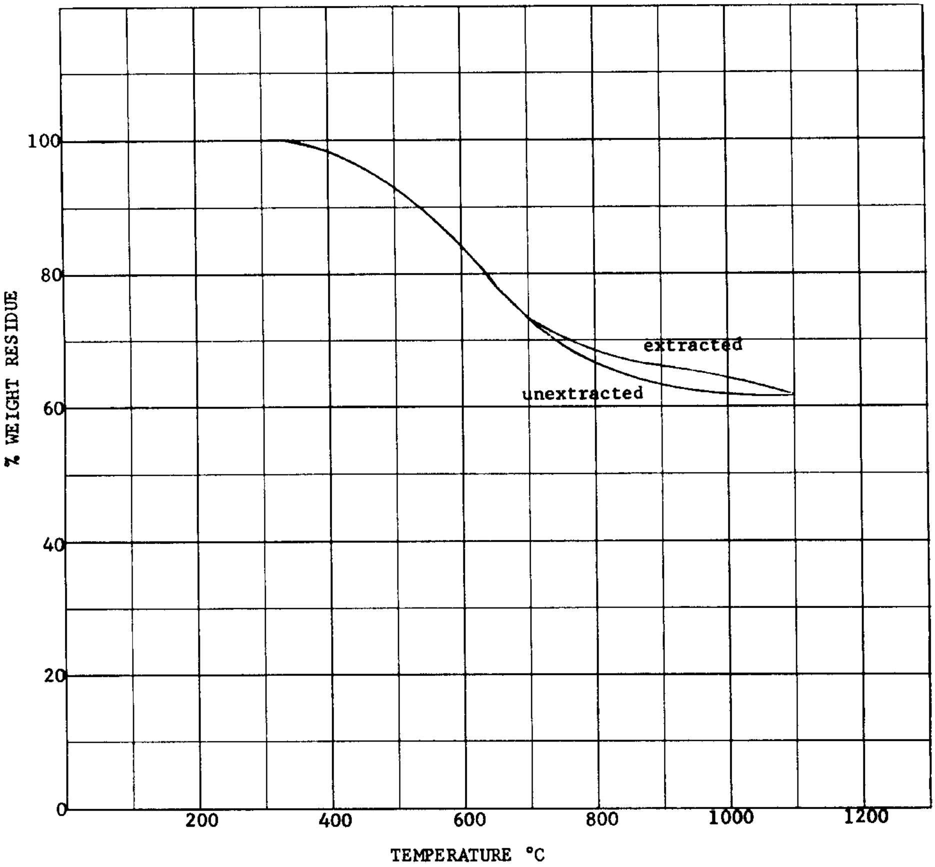
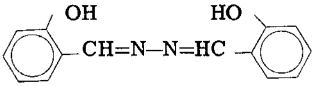


FIG. 15. Thermogram in nitrogen of polymeric residue obtained from decomposition of  .

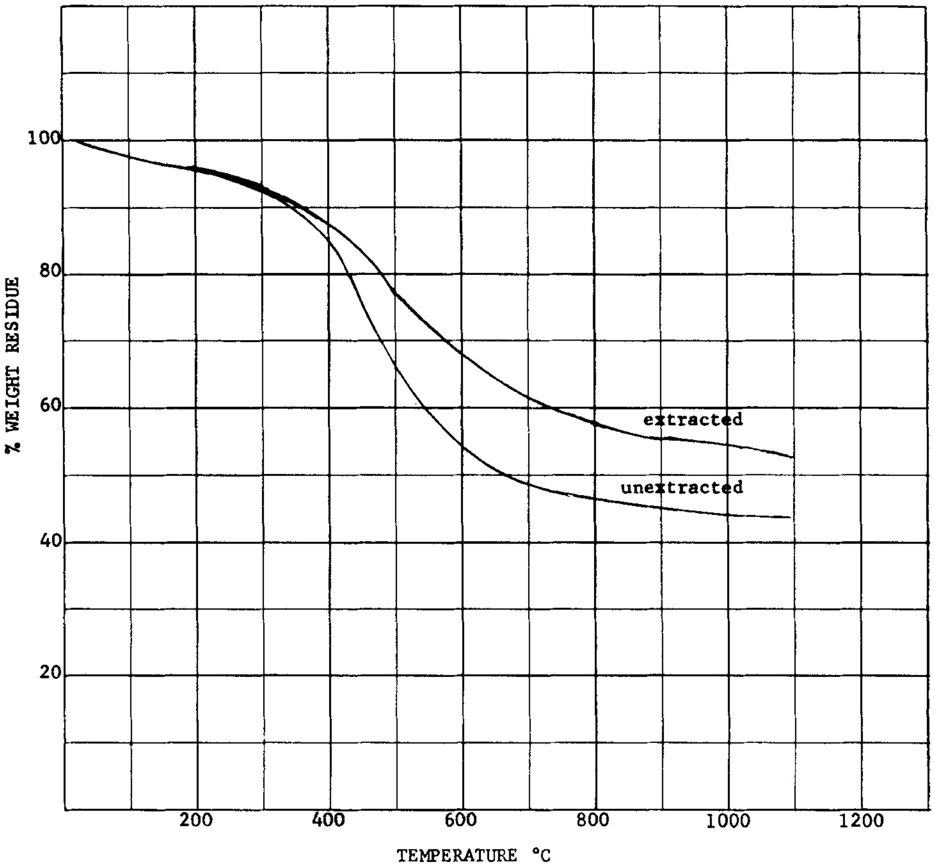
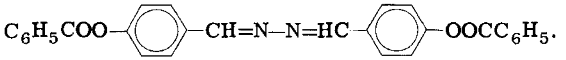


FIG. 16. Thermogram in nitrogen of polymeric residue obtained from decomposition of



Downloaded At: 11:34 25 January 2011

The elemental analyses for the crude and extracted polymeric residues were as follows:

Polymer from (II), crude, found: C, 75.74; H, 3.57; N, 10.93; O, 9.76
extracted, found: C, 74.93; H, 4.99; N, 5.28; O, 14.80

Calculated for $C_7H_5NO_2$: C, 62.22; H, 3.70; N, 10.37; O, 23.70
C_7H_5NO: C, 70.59; H, 4.20; N, 11.76; O, 13.45
$C_{14}H_{10}NO_2$: C, 75.00; H, 4.46; N, 6.25; O, 14.28

Polymer from (III), crude, found: C, 74.12; H, 5.09; N, 5.74; O, 15.05
extracted, found: C, 73.18; H, 5.21; N, 5.68; O, 15.93

Calculated for C_7H_6O: C, 79.22; H, 5.70; N, 0.00; O, 15.08
$C_{14}H_{10}NO_2$: C, 75.00; H, 4.46; N, 6.25; O, 14.28
$C_{14}H_{10}N_2O$: C, 75.66; H, 4.54; N, 12.61; O, 7.20
C_7H_5NO: C, 71.78; H, 4.30; N, 10.25; O, 13.66

Polymer from (IV), crude, found: C, 78.36; H, 4.03; N, 4.52; O, 13.09
extracted, found: C, 77.96; H, 4.14; N, 6.25; O, 11.66

Calculated for C_7H_6O: C, 79.22; H, 5.70; N, 0.00; O, 15.08
$C_{14}H_{10}NO_2$: C, 75.00; H, 4.46; N, 6.25; O, 14.29
$C_{14}H_{10}N_2O$: C, 75.66; H, 4.54; N, 12.61; O, 7.20
C_7H_6NO: C, 71.78; H, 4.30; N, 10.25; O, 13.66

Polymer from (X), crude, found: C, 79.86; H, 4.48; N, 1.53; O, 14.13
extracted, found: C, 76.26; H, 5.85; N, 7.14; O 10.75

Calculated for $C_{14}H_{10}O_2$: C, 80.00; H, 4.76; N, 0.00; O, 15.24
$C_{14}H_{10}NO_2$: C, 75.00; H, 4.46; N, 6.25; O, 14.29
$C_{14}H_{12}NO$: C, 80.00; H, 5.72; N, 6.66; O, 7.62

Decomposition in the Presence of Lewis Acids

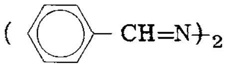
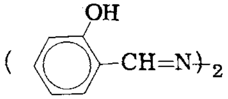
The onset decomposition temperatures in nitrogen of dibenzylidene azine and of di-(o-hydroxybenzylidene)-azine, respectively,

Downloaded At: 11:34 25 January 2011

Downloaded At: 11:34 25 January 2011

in the presence of 1, 5, and 10 wt. % of p-toluenesulfonic acid and zinc chloride, respectively, are given in Table 2 and illustrated in Fig. 17.

TABLE 2. Decomposition Temperatures of Some Monomeric Azomethines in the Presence of Lewis Acids

	Onset decomposition temperature (°C) in nitrogen	
% Catalyst[a]		
None	306	335
1% TSA	302	325
5% TSA	294	308
10% TSA	273	286
1% $ZnCl_2$	300	328
5% $ZnCl_2$	283	311
10% $ZnCl_2$	260	296

[a] TSA, p-toluenesulfonic acid.

Kinetics of the Decomposition of Molten Monomeric Azines

Isothermal Decomposition. A modification of the procedure described [8] by Williams and Lawrence was used. The apparatus consisted of a bottom-sealed quartz reactor tube, 1 cm in diameter, of approximately 50 ml capacity. The top of the tube was fitted by means of a standard-taper ground-glass joint to a two-way stopcock, one opening of which was attached to a source of deoxygenated nitrogen and the other opening to a gas buret filled with distilled water to absorb soluble gas so that only the volume of the water-insoluble permanent gases was recorded. The gas buret was equipped with a venting cock. The procedure consisted in charging the reactor tube with sample, attaching it to the apparatus, sweeping out the apparatus with deoxygenated nitrogen, and then inserting the reactor tube in a tightly fitting drilled hole in a 3 × 3 in. aluminum block which was preheated to the midpoint decomposition temperature given in Table 1; the temperature was thermostatically controlled to ±1°C by a ProportioNull Controller.

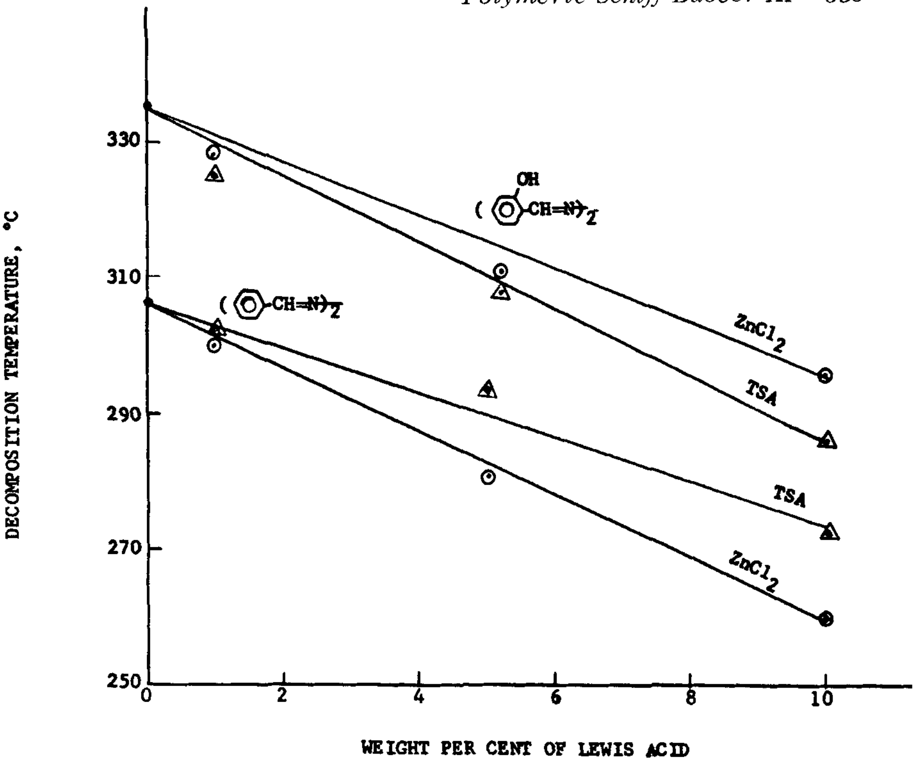
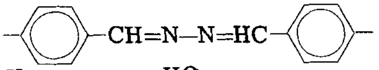
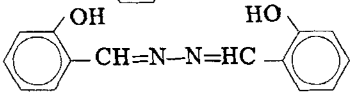


FIG. 17. Effect of Lewis acids on the decomposition temperatures of



and



.

The level of the molten azine was always below the level of the heated aluminum block. Time and volume readings were started with the insertion of the reactor tube in the heated block. The volume of gas was recorded as a function of time in minutes. When the evolution of gas ceased, the reactor tube was removed from the block and allowed to equilibrate to about 25°C, and the final volume of the gas, after appropriate corrections for temperature and pressure, was converted to mole per cent theory of nitrogen. The method [8] of Williams and Lawrence was used to calculate the velocity coefficients, which are recorded in min^{-1}.

Downloaded At: 11:34 25 January 2011

Downloaded At: 11:34 25 January 2011

The crude reaction products in most cases were separated qualitatively according to the methods given [9] by Zimmerman and Somasekhara, and the presence of the stilbenes and the nitriles confirmed in the decomposition products. There were identified: stilbene, m.p. 123–124°C, lit. [15] 124°C; 2, 2′-dihydroxystilbene, m.p. 91–92°C, lit. [15] 92°C; 4, 4′-dihydroxystilbene, m.p. 281°C, lit. [15] 281°C; 2, 2′-dichlorostilbene, m.p. 97°C, lit. [15] 97°C; 4, 4′-dinitrostilbene, m.p. 210–211°C, lit. [15] 212°C; benzonitrile, b.p. 190°C, lit. [15] 190.7°C; 2-hydroxybenzonitrile, m.p. 98°C, lit. [15] 98°C; 4-hydroxybenzonitrile, m.p. 112°C, lit. [15] 113°C; 4-nitrobenzonitrile, m.p. 130°C, lit. [15] 131°C; 2-methoxybenzonitrile, m.p. 24°C, lit. [15] 24.5°C; 2-chlorobenzonitrile, m.p. 38°C, lit. [15] 39.5°C; 4-chlorobenzonitrile, m.p. 94°C, [15] 96°C; 4-fluorobenzonitrile, m.p. 34°C, lit. [15] 34.8°C.

The presence of ammonia in the distilled water in the gas buret was detected by titration with standard acids and confirmed by the addition of concentrated sodium hydroxide to the aqueous solution causing the liberation of ammonia.

Ambient-Temperature System. An ambient-temperature method was also used to determine the per cent theory of nitrogen obtained by the decomposition of the azines. The apparatus used was identical to that used in the isothermal method. The procedure consisted in charging the reactor as in the above experiments, then inserting the charged reactor tube into the aluminum block at 25°C and heating the mass at a rate of approximately 8°C/min up to the midpoint decomposition temperature, at which it was held until gas evolution ceased. The volume of gas collected, after appropriate corrections, was converted to mole per cent theory of nitrogen.

The relative data are shown in Table 3, and the graphical representations from which the isothermal velocity constants were derived are shown in Figs. 18 to 27.

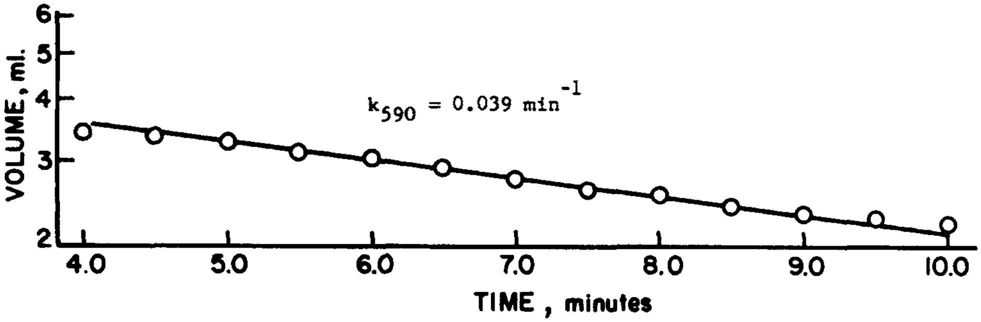


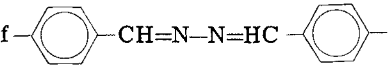
FIG. 18. Plot of ln C (volume of N_2) as a function of time for the decomposition of  at 590°K.

TABLE 3. Data on Melt Decomposition of Some Monomeric Azines

	Isothermal decomposition		Ambient decomposition		Isothermal values of $k_t = \text{min}^{-1}$		
Azine	used	Corr. % N_2	g used	Corr. % N_2	t^a	min^{-1}	Fig. No.
I	0.4081	76.0	4.2304	74.9	590	0.039	18
II	0.2185	64.2	0.3089	84.2	593	0.153	19
III	0.4029	45.7	4.0500	52.0	568	0.426	20
IV	0.4000	38.8	3.4713	14.2	628	0.584	21
V	0.0995	92.4	3.3113	90.5	583	0.034	22
VI	0.4056	80.6	0.3357	72.4	583	0.099	23
VII	0.3994	63.5	2.1558	69.8	592	0.264	24
VIII	0.4058	71.3	0.3352	69.1	588	0.022	25
IX	0.3149	24.9	0.4458	27.2	558	0.082	26
X	0.2637	53.7	0.3241	55.5	608	0.051	27

[a] t = absolute temperature.

Downloaded At: 11:34 25 January 2011

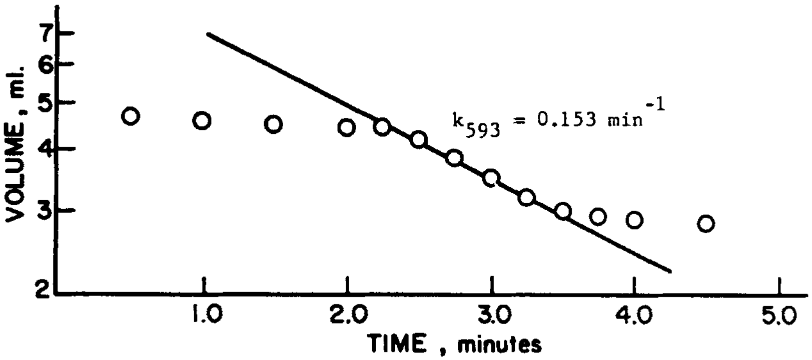
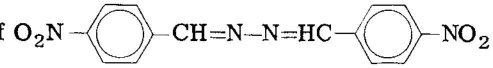


FIG. 19. Plot of ln C (volume of N_2) as a function of time for the decomposition of  at 593°K.

Downloaded At: 11:34 25 January 2011

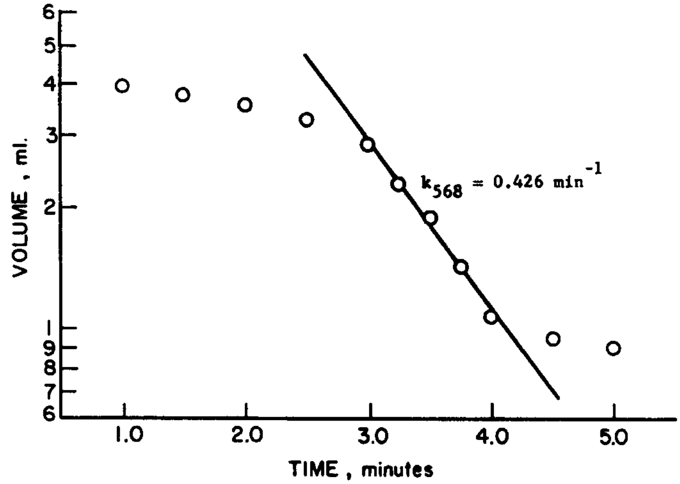
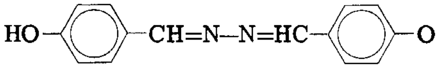


FIG. 20. Plot of ln C (volume of N_2) as a function of time for the decomposition of  at 593°K.

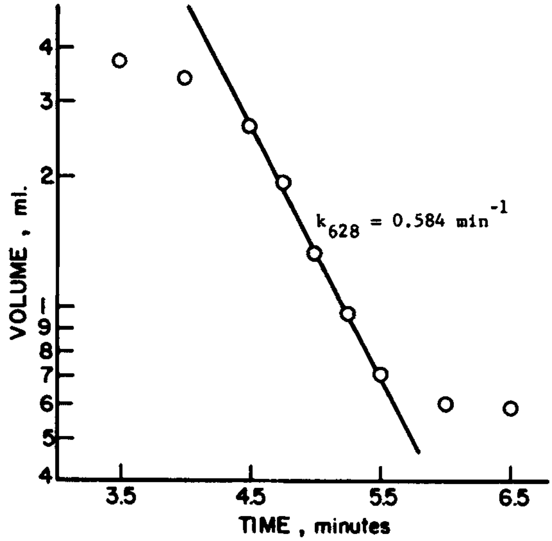
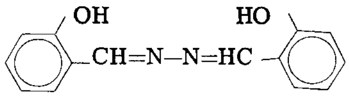


FIG. 21. Plot of ln C (volume N_2) as a function of time for the decomposition of  at 628°K.

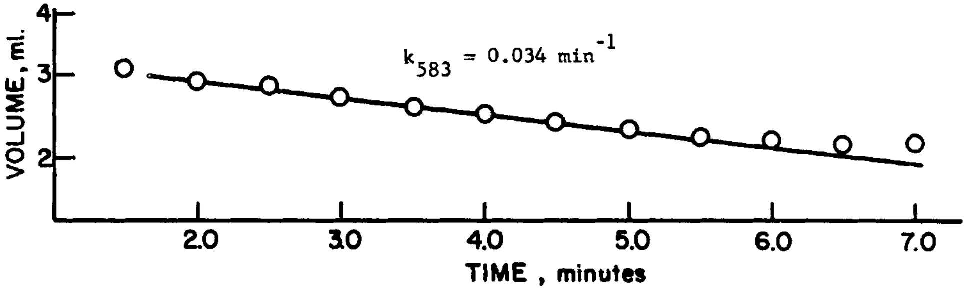
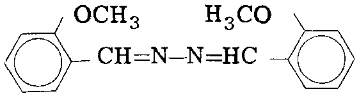


FIG. 22. Plot of ln C (volume N_2) as a function of time for the decomposition of  at 583°K.

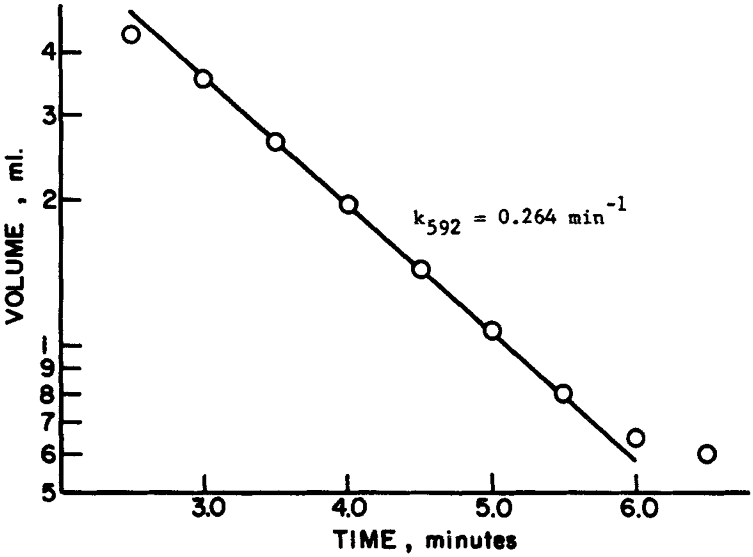
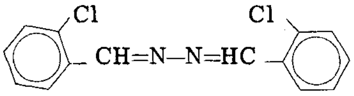


FIG. 23. Plot of ln C (volume of N_2) as a function of time for decomposition of  at 592°K.

Downloaded At: 11:34 25 January 2011

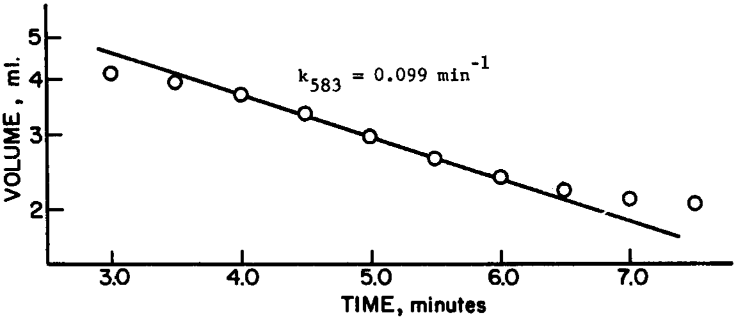
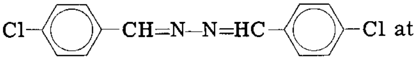


FIG. 24. Plot of ln C (volume of N_2) as a function of time for the decomposition of  583°K.

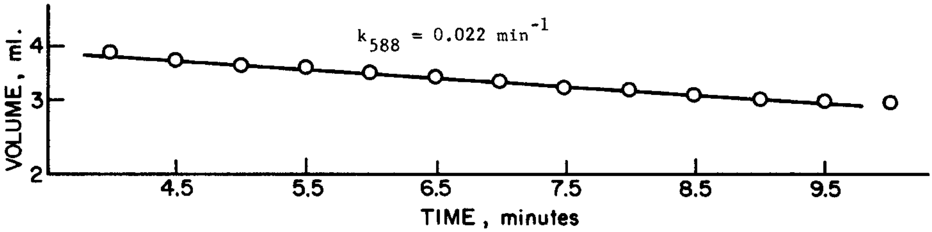
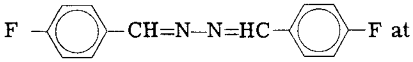


FIG. 25. Plot of ln C (volume of N_2) as a function of time for the decomposition of  588°K.

Downloaded At: 11:34 25 January 2011

Downloaded At: 11:34 25 January 2011

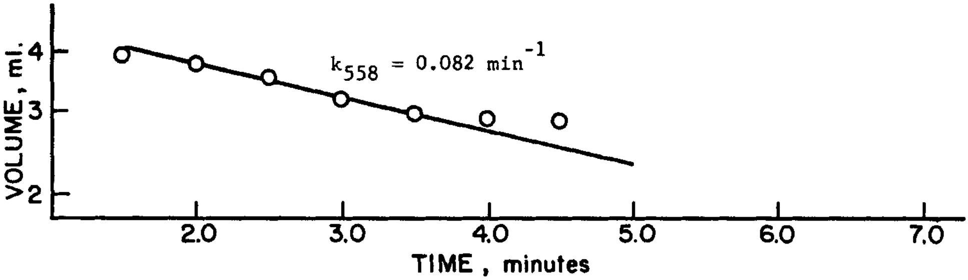
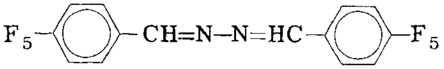


FIG. 26. Plot of ln C (volume of N_2) as a function of time for the decomposition of  at 558°K.

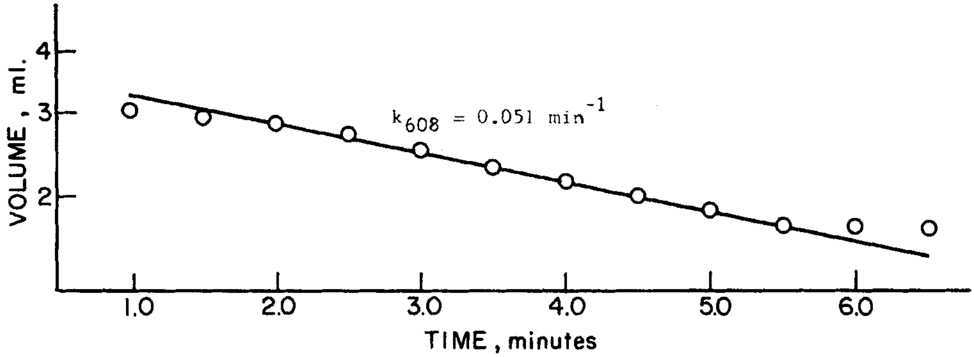
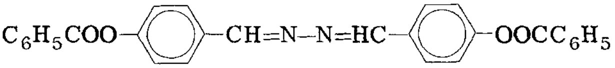


FIG. 27. Plot of ln C (volume of N_2) as a function of time for the decomposition of

 at 608°K.

Downloaded At: 11:34 25 January 2011

Exchange Reactions

Aldehyde Exchange. (a) Dibenzylideneazine, 2.08 g (0.01 M), and p-chlorobenzaldehyde, 3.09 g (0.02 M), were mixed together in a microflask equipped with a reflux condenser and the mixture heated under a deoxygenated nitrogen atmosphere, at 185°C for 2 hr; then the mixture was distilled at 600 mm Hg pressure while maintaining the flask temperature at 180°C, and there was recovered 0.87 g (38%) of benzaldehyde. The residue in the flask was recrystallized from benzene–ethanol and there was obtained 2.05 g (74%) of p-(ClC$_6$H$_4$CH=N$-)_2$, m.p. 210°C; mixed m.p. with authentic sample, 210°C.

(b) Dibenzylideneazine, 2.08 g (0.01 M), and o-methoxybenzaldehyde, 3.0 g (0.02 M), were reacted as above and there was isolated 0.42 g (84%) of benzaldehyde and 2.04 g (72%) of o-CH$_3$OC$_6$H$_4$CH=N$-)$ m.p. 143°C; mixed melt with authentic sample, 143°C.

Amine Exchange. (a) A mixture of 7.24 g (0.04 M) of benzylideneaniline and 0.753 g (0.02 M) of hydrazine (85% in water) was refluxed for 1 hr; then the mixture was distilled at 700 mm Hg pressure and the benzylideneaniline was recovered substantially unchanged.

(b) A mixture of 14.48 g (0.08 M) of benzylideneaniline and 1.52 g (0.04 M) of hydrazine (85% in water) was mixed in a ground-glass flask and placed in a refrigerator at 5°C for 7 days, during which time a precipitate formed which was removed by filtration and recrystallized from ethanol and there was obtained 0.92 g (11%) of dibenzylideneazine, m.p. [13] 94°C.

Bis Exchange. (a) A mixture of 4.16 g (0.02 M) of dibenzylideneazine and 8.62 g (0.04 M) of p-chlorobenzylideneaniline was heated under nitrogen at 180°C for 2 hr; then the mixture was distilled at 15 mm Hg pressure while maintaining the flask temperature at 180°C, and two fractions were collected: the first fraction, 4.42 g, contained mostly benzylideneaniline (61%) of theory and the second fraction, 2.93 g, contained mostly unconverted (34%) p-chlorobenzylideneaniline. The residue was recrystallized from benzene–ethanol and there was isolated 2.98 g (54%) of di-(p-chlorobenzylidene)-azine, m.p. 213°C.

(b) A mixture of 4.16 g (0.02 M) dibenzylideneazine and 8.62 g (0.04 M) of p-chlorobenzylideneaniline was heated under nitrogen at 350°C for 1 hr and the mixture distilled at 15 mm/Hg to remove volatile molecules. The residue was recrystallized from 95% ethanol. Benzonitrile, p-chlorobenzonitrile, benzylideneaniline, stilbene, p, p′-dichlorostilbene, and unidentified products were isolated from the reaction product.

Acetal Reactions. (a) Benzylidenediethyl ether, 7.21 g (0.04 M) and anhydrous hydrazine, 0.64 g (0.02 M) were placed in a microflask equipped with a reflux condenser and reacted at 80°C for 2 hr;

then the mixture was evaporated to dryness at 15 mm Hg and the solid residue recrystallized from 95% ethanol. There was obtained 3.78 g (91%) of dibenzylideneazine, m.p. 94°C.

(b) Benzylidenedibutyl ether, 9.24 g (0.04 M), and anhydrous hydrazine, 0.64 g (0.02 M), were reacted as in the experiment above at 90°C for 3 hr and there was obtained 3.70 g (89%) of dibenzylideneazine, m.p. 94°C.

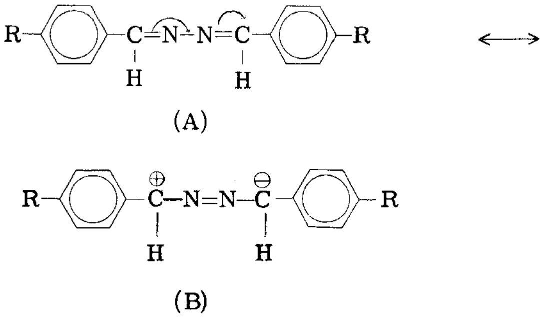
(c) p-Chlorobenzylidenediethyl ether, 8.58 g (0.04 M), and anhydrous hydrazine, 0.64 g (0.02 M), were reacted in the above experiment at 80°C for 2 hr and there was obtained 5.11 g (93%) of di-(p-chlorobenzylidene)-azine, m.p. 213°C.

(d) p-Chlorobenzylidenediethyl ether, 8.58 g (0.04 M), and dibenzylideneazine, 4.16 g (0.02 M), were heated under nitrogen at 175°C for 3 hr; then the mixture was distilled at 15 mm Hg while maintaining the flask temperature at 175°C, and benzylidenediethyl ether, 4.90 g (68%), was collected as a distillate. The residue was recrystallized from alcohol and there was obtained 3.38 g (61%) of di-(p-chlorobenzylidene)-azine, m.p. 213°C.

Downloaded At: 11:34 25 January 2011

DISCUSSION

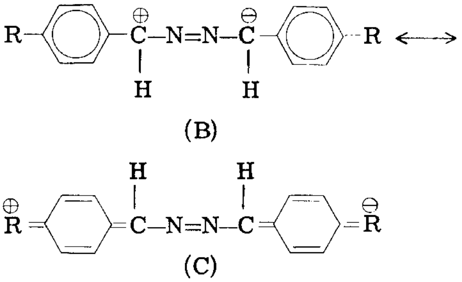
The onset of decomposition for monomeric azines I–X was observed in the temperature range 262–335°C; the highest temperature, 335°C, was found for IV, the di-(o-hydroxybenzylidene)-azine. If IV is temporarily excluded, the range is 262–308°C; this is a relatively narrow range of 46°C for the nine different azines, which reflect diverse substitutions in the ortho and the para positions of the benzylidene moiety as well as differences in the chemical nature of the substituents. This would tend to confirm the decomposition mechanism proposed [9] by Zimmerman and Somasekhara—that the rupture occurs in the common azine moiety to yield a carbene and an aryldiazomethane. They do not delineate any intermediate steps in the splitting of this molecule; it is most probable that the splitting occurs from an excited electron state of the azine, thus:



(11)

Downloaded At: 11:34 25 January 2011

Also, charge interaction with the aromatic rings will vary with the electronic nature of the substituent, (R), so that resonance form (B) can assume that of form (C):



(12)

A qualitative agreement was observed between the decomposition temperatures and the electronic character of the substituent, as shown in Table 4. For example, a higher stability was contributed to the azine by the p-nitro substituent in II than by the p-hydroxyl substituent in III, and more energy, namely, a higher temperature, 306°C, was required to cause the fission of II than the 285°C found for III. Also, the azines with substituents of a positive electronic nature decomposed at higher temperatures than those in which the substituents were electronegative. Substituents in the ortho positions tended to lower the energy required, and hence lower temperatures, for the decomposition of the azine. Thus the o-chloro derivative, VI, decomposed at a lower temperature, 292°C, than the temperature of 312°C found for the p-chloro derivative VII; and the o-methoxy derivative, V, decomposed at 265°C, which is lower than the temperature of approximately 300°C reported [9] by Zimmerman and Somasekhara for the p-methoxy derivative.

There are two apparent exceptions to the above generalization that may be observed in Table 4, namely, the decomposition temperature of the perfluoro derivative, IX, and of the o-hydroxy derivative, IV. The lower decomposition temperature, 262°C, of IX compared to 306°C for the p-fluoro derivative, VIII, is attributable readily to the high reactivity of the p-fluorine atom in the perfluoromonosubstituted benzenes compared to the relative stability of the mono-, di-, tri-, and tetrafluoro-substituted benzenes [16–18]. The o-hydroxy derivative among those investigated in this study, was highest at 335°C in the scale of decomposition temperatures. This high stability against decomposition can be attributed to hydrogen bonding of the phenolic hydrogen with the azine nitrogen:

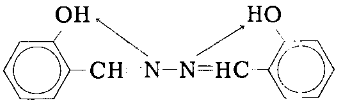
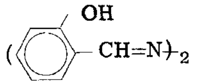
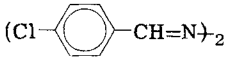
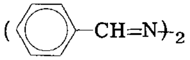
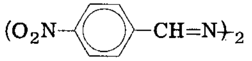
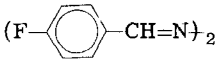
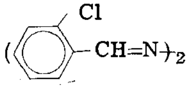
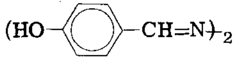
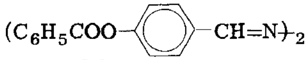
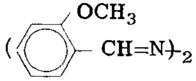
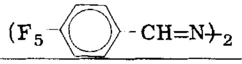


TABLE 4. Relationship of Decomposition Temperature of Azines and Their Substituents

Monomer	Decomposition temp., °C	Structure	Substituent	Electronic nature
IV	335		—OH	⊖
VII	312		—Cl	⊕
I	306		—H	Neutral
II	306		$-NO_2$	⊕
VIII	306		—F	⊕
VI	292		—Cl	⊕
III	285		—OH	⊖
X	275		$-OOCC_6H_5$	⊖
V	265		$-OCH_3$	⊖
IX	262		$-F_5$	⊕

evidence for which is seen in its infrared spectrum shown in Fig. 7 by the broad O—H stretching band in the region 3000 cm^{-1}. Polymeric azines possessing o-hydroxy substitution also show added stability as a contribution from hydrogen bonding [1]. Supporting evidence is found by comparison of the o-hydroxy derivative with the o-chloro derivative, VI, which decomposes at 292°C, and with o-methoxy derivative, V, which decomposes at 265°C; in both these cases hydrogen bonding is lacking in these compounds. It appears, therefore, that the temperature of decomposition of the monomeric azines, $(R-C_6H_4CH{=}N)_2$, is dependent to some extent upon the

Downloaded At: 11:34 25 January 2011

Downloaded At: 11:34 25 January 2011

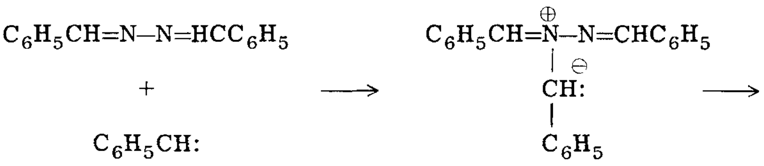
electronic character of the substituent, R, the contributing resonance structures, and the presence of hydrogen bonding to the azine moiety.

All the monomers, I–X, liberated nitrogen when decomposed; none of them liberated the theoretical quantity of nitrogen. This is in accord with previous observations [8, 9, 19-21]. Williams and Lawrence reported [8] nitrogen yields from the decomposition of I in the range 333–335°C of from 12.2 to 75.0% of the theoretical value, while Zimmerman and Somasekhara obtained [9] an 83% yield of nitrogen at 300°C. These values contrast with the results of this study for I of 76% nitrogen at an isothermal temperature of 317°C, and 74.9% under ambient decomposition temperatures. Lower than theoretical nitrogen yields were also reported [9] for other azines; 80% at 300°C for di-(p-methylbenzylidene)-azine and 88% at 300°C for di-(p-methoxybenzylidene)-azine. In this study, the yield of nitrogen for the di-(o-methoxybenzylidene)-azine was 92.4% at 310°C. By-products have been detected by previous workers in the decomposition of aldazines. Benzonitrile [9, 19], ammonia [8, 19], phenanthrene [20], and complex nitrogen compounds such as 2, 4, 5-triphenylimidazole [9, 20] have been detected among the by-products. The presence of by-products such as nitriles and ammonia was also confirmed qualitatively in this study for the monomers investigated. However, the yields of nitrogen for the 10 aldazines, as shown in Table 3, ranged from 24.9 to 92% of the theoretical values, whereas the yields of nitrogen from the relatively simple azines of the previous studies [8, 9] ranged from 75 to 88% of the theoretical values. The nitrogen values found in this work for dibenzylidene azine, I, di-(o-methoxybenzylidene)-azine, V, and di-(o-chlorobenzylidene)-azine, III, are generally in fair agreement with those of previous studies. The yield of nitrogen from the seven azines II–IV and VII–X, however, are lower and fall in the range 24.9–71.3%. When the value of 24.9% is excluded for IX because of the added complication introduced by the polyfluoraryl moiety, the range of nitrogen values becomes 38.8–71.3% for II, III, IV, VII, VIII, and X. All these azines contain substituents which appear, as shown above, to influence their decomposition temperatures as contributions to resonance structures, and, in the case of the o-hydroxy substituent, an additional contribution is made by the presence of hydrogen bonding. The observation that the yields of nitrogen change dramatically with substitution would indicate that the electronic character of the substituent also plays some part in their decompositions. The additional observations that the decomposition temperatures change with substitution and that the theoretical yield of nitrogen was not obtained from any of the 10 azines would seem to indicate that secondary processes, other than that involving the aryl diazomethane ion chain reaction of Eqs. (3)–(5), may be operative. The kinetics of the decomposition

Downloaded At: 11:34 25 January 2011

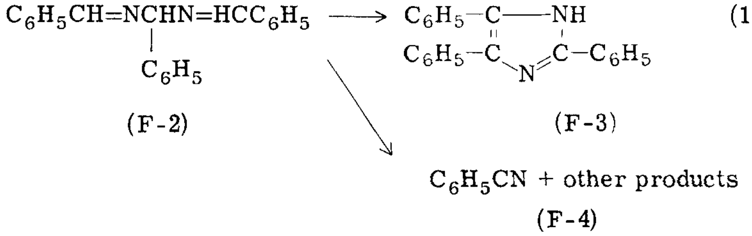
was shown [8] to be first order for dibenzylidene azine within the range 30–80% decomposition; some minor deviation from the linearity of the plots of log c versus t were found [8] in some cases at the beginning and at the end of the reaction. Our studies have confirmed the existence of first-order kinetics in the decomposition for dibenzylidene azine as well as for the other azines, II–X. However, the decomposition reaction did not appear to follow first-order kinetics throughout the entire reaction; deviations were observed for various periods of time at the beginning of the reaction, which was followed by a period whose slope indicated a first-order reaction, and this in turn was followed by another period whose order of reaction, in a plot of 1/c versus time, indicates an order other than 1. Side reactions appear to account for these deviations.

An attempt was made in these studies to use the thermogravimetric analytical method of Freeman and Carroll [22] in the du Pont thermogravimetric apparatus, to determine the kinetics and order of the decomposition of the various azines. This attempt was unsuccessful, since the rate of loss of weight due to sublimation or evaporation far exceeded, and hence masked, any weight loss due to decomposition. This method was successfully applied, however, to the polymeric azines, and the order of the decompositions was found [1] in a number of decompositions to be fractionally higher than 1, varying from 1.08 to 1.32. Evidence of this kind tends to strengthen the postulate that the decomposition is not exclusively through the aryldiazomethane ion chain reaction, which also does not appear to explain thoroughly the existence of by-products or the low yield of nitrogen. Also to be explained is the observation [8] that the decomposition of dibenzylideneaniline has the relatively high N_2/NH_3 ratio of approximately 9. It has been considered [9] uncertain in the decomposition of dibenzylideneazine whether benzonitrile and triphenylimidazole were derived from reactions of the phenylcarbene formed in the initiation process, or from the termination step, or from independent reactions. It was proposed [9] that an attack of the phenylcarbene on the dibenzylidene azine could form an intermediate (F-1) which could rearrange to dihydrobenzamide (F-2), which is known [21] to yield triphenylimidazole (F-3), or which possibly by β-elimination could afford benzonitrile as one of the products:



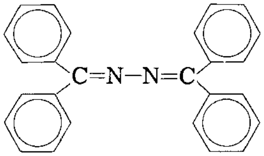
$$C_6H_5CH{=}N{-}N{=}HCC_6H_5 + C_6H_5CH: \longrightarrow C_6H_5CH{=}\overset{\oplus}{N}(\overset{\ominus}{C}H{:}\,C_6H_5){-}N{=}CHC_6H_5 \longrightarrow$$

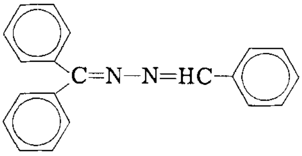
(F-1)



(13)

The reactions of Eq. [13], however, do not account for the presence of ammonia in the by-products. A more plausible explanation appears to be found in the current publication [23] of Hirsch, who reported on the pyrolysis of (XI) benzophenone azine [(di-benzhydrylidene)-azine] and (XII) benzhydrylidene-benzylidene-azine over a temperature range 375–500°C.


(XI)


(XII)

Downloaded At: 11:34 25 January 2011

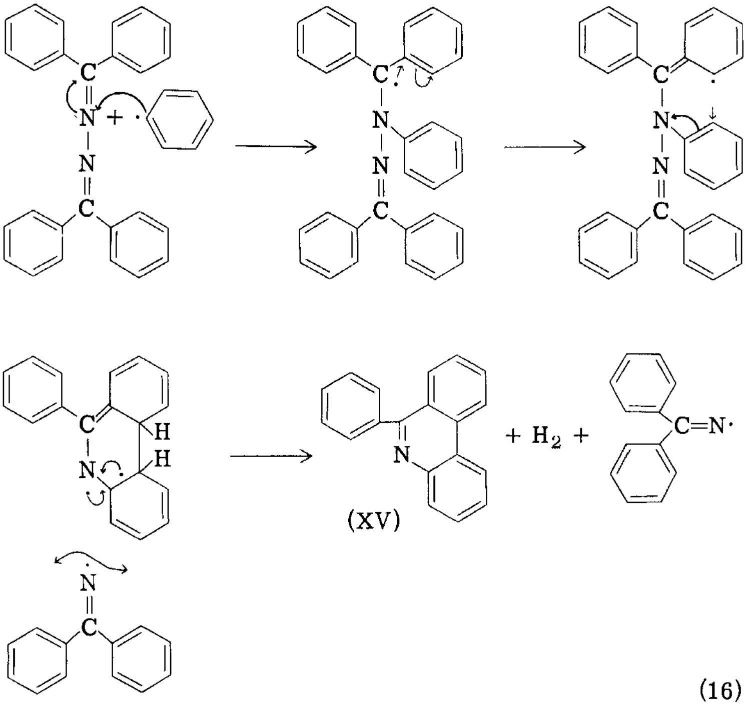
It was shown [23] that XI decomposed by a free-radical process to yield principally benzonitrile, benzhydrylideneimine, and 6-phenylphenanthridine, accompanied by lesser quantities of benzene, biphenyl, diphenylmethane, and benzhydrylidene aniline; only a trace of nitrogen, but no tetraphenylethylene, was found. The reaction scheme proposed involved the scission of XI into two benzhydrylideneinoradicals and not to the carbene and the diazomethane. Accordingly, it was concluded that scission [Eq. (14)] to the carbene and the aryldiazomethane was not the controlling mechanism:

$$(C_6H_5)_2C{=}N{-}N{=}C(C_6H_5)_2 \rightleftharpoons (C_6H_5)_2C: + (C_6H_5)_2C{-}\overset{\ominus}{N}{\equiv}\overset{\oplus}{N}: \tag{14}$$

A reasonable explanation for the failure of the aryldiazomethane mechanism to participate during the pyrolysis is on steric grounds, and the pyrolysis is forced to take another course in which there are no steric restrictions. The reaction scheme proposed involved the scission [Eq. (15)] of XI into two benzhydrylideneimino radicals (XIII) as the product of rupture of the N–N bond. The radicals XIII are the source of benzonitrile, phenyl radicals, and benzhydrylideneimine.

$$\begin{tikzcd}
\underset{\text{(XI)}}{(C_6H_5)_2C{=}N{-}N{=}C(C_6H_5)_2} \arrow[r, "\Delta"] & \underset{\text{(XIII)}}{2(C_6H_5)_2C{=}N\cdot} \arrow[dl] \arrow[d, "\text{source of H}"] \\
C_6H_5C{\equiv}N + C_6H_5\cdot & \underset{\text{(XIV)}}{(C_6H_5)_2C{=}NH}
\end{tikzcd} \tag{15}$$

The reaction of phenyl radicals with XIV is followed by rearrangement and an elimination to afford 6-phenylphenanthridine, XV, and hydrogen with the regeneration of the benzhydrylideneimino radical [Eq. (16)].



(16)

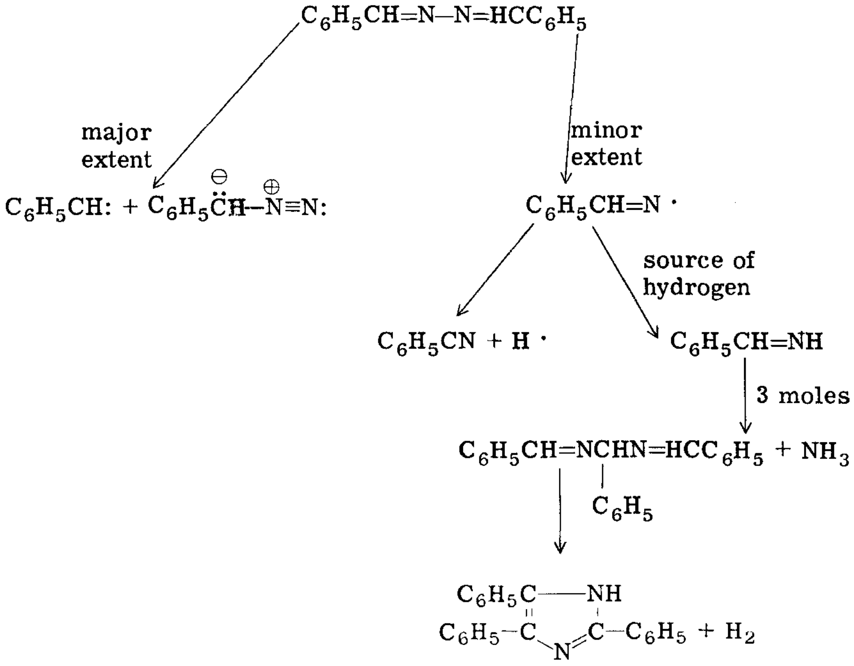
From the dual source of benzhydrylidenimino radicals, only those which do not form benzhydrylidenimine are the source of phenyl radicals which participate in the formation of XV, in which case the molar quantity of XV cannot exceed that of benzonitrile; this speculation was confirmed by chromatographic analyses of the products. This radical mechanism was shown [23] to account

Downloaded At: 11:34 25 January 2011

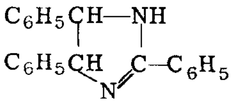
Downloaded At: 11:34 25 January 2011

for all the products of thermolysis. Since this is an entirely different course that the ionic mechanism proposed for the aldazines, the thermolysis of the half aldazine–half ketazene (XII) was investigated. In this case, the products of pyrolysis consisted of nitrogen, benzene, benzonitrile, biphenyl, diphenylmethane, fluorene, benzhydrylidene imine, phenanthridine, triphenyl ethylene, 6-phenylphenanthridine, and some higher-boiling components which were not resolved but which probably contained [23] 2, 4, 5-phenylimidazole. The behavior of this mixed azine led to the conclusion that both the radical and the ionic mechanisms were participating to a major extent.

It was also proposed [23] that both the ionic and the radical mechanisms are operative in the thermolysis of dibenzylidene azine, but that the radical mechanism participates to a lesser extent. The ionic mechanism explains the production of nitrogen and stilbene, whereas the radical mechanism accounts for the presence of benzonitrile and 2, 4, 5-triphenylimidazole, as well as of ammonia:



The benzalimine, $C_6H_5CH{=}NH$, is an unstable compound which converts, with the elimination of ammonia to dihydrobenzamide, which is known [21, 24] to cyclize through the intermediate amarine,



to 2, 4, 5-triphenylimidazole. It seems reasonable to assume that substitutions on the benzene ring of the dibenzylidene azine which change the electronic factors in the azine with regard to decomposition temperatures would also change the relative ratio of the extents of the ionic and radical mechanisms; this ratio would be evident to some extent by the change in the amount of nitrogen liberated since the radical mechanism does not account for the production of nitrogen, but does explain the presence of the nitrile and ammonia. This appears to be the case in this study and it was qualitatively observed that when the yield of nitrogen was low, the yield of ammonia was higher than the approximately 9:1 ratio observed for the dibenzylidene azines. In agreement with others [8, 9], it was also observed that the mole per cent yield of the stilbene was also less than that of the nitrogen yield. Some typical values are shown in Table 5. This would seem to indicate a loss of C_6H_5CH structures either from C_6H_5CH: or $C_6H_5\overset{\ominus}{C}H{-}N{\equiv}\overset{\oplus}{N}$: by reaction with ammonia, which at pyrolysis temperatures would yield the nitrile through a benzylamine intermediate. Reaction of ammonia with either fragment would not decrease the nitrogen yield but would decrease the stilbene yield. However, since the concentration of C_5H_5CH: in the ionic mechanism is low, it is more reasonable to assume that the reaction involves the diazomethane ion. Less pro-

TABLE 5. Ratio of Products from Decomposition of Some Monomeric Azines

	Mole %			
Azine	Nitrogen	Stilbene	Nitrile	Imidazole
$(C_6H_5CH{=}N)_2$ [8]	75	65	4	a
$(C_6H_5CH{=}N)_2$ [9]	83	61	20	5
$(C_6H_5CH{=}N)_2$	74.9	65	5	a
$(p\text{-}CH_3OC_6H_4CH{=}N)_2$ [9]	88	35	33	a
$(p\text{-}CH_3C_6H_4CH{=}N)_2$ [9]	80	38	26	a

[a] Not isolated, but high-boiling compounds shown to be present.

Downloaded At: 11:34 25 January 2011

bable is the trimolecular reaction of two molecules of the carbene, $C_6H_5CH\colon$, with one molecule of the benzhydrylidenimino radical to yield a dihydrobenzamide both on kinetic grounds and on concentration terms.

An energy of activation of 53, 000 cal/mole was found [8] for the decomposition of dibenzylidene azine, I, with values for k_1 of 0. 044 at 591°K and 0. 134 at 608°K compared to the values of 0. 039 at 590°K and 0. 061 at 597°K found in these studies, which yield an activation energy of 40, 000 cal/mole. This activation energy would be expected to change with substitution on the aromatic rings in the azine. For $(HO-C_6H_4-CH=N)_2$, III, k_1 at 568°K was 0. 426 min^{-1}, and at 588°K k_1 was found to be 0. 620 min^{-1}, which yield a value for E of 27, 000 cal/mole. Energies of activation of this order of magnitude varying from 37 to 67 cal/mole have also been found [1] for polymeric azines of various structures.

Another interesting observation made in the course of this study was that the substituted monomeric azines, II, III, IV, and X, on decomposition, produced glassy, hard, black polymeric substances which were insoluble in common solvents, dimethylacetamide, and concentrated sulfuric acid. The infrared spectra of the extracted polymers, Figs. 9–12, present similar profiles, which may indicate similar or related structures derived by a common polymerization mechanism. The spectra of these polymers are similar in many respects to those of the phenol-formaldehyde condensation products [25], which have methylene bridges between aromatic rings. Since the monomers were disubstituted benzenes, it would be expected that trisubstituted benzene structures would be evident readily in the spectra of these polymers. The bands at 820 cm^{-1} found in the polymers from II, III, and X are attributable [2] to 1, 4 disubstitution in a benzene ring, and this implies that the polymers are substantially linear. The band at 752 cm^{-1} found in the polymer from IV is attributable to 1, 2 disubstitution; this would imply also that the polymer is substantially linear. However, the insolubility of these polymers indicates that there is at least some measure of cross-linking.

Bands in the 750- and 820-cm^{-1} regions have also been assigned to 1, 2, 4-, o-1, 2-, and 1, 2, 3, 4-type aromatic substitution [2], and thus the bands responsible for cross-linking may be obscured in the spectra. Although it was not a purpose of this study at this time to elucidate the structure of these polymers or the mechanism by which they are derived, it was expected that some information would be obtained from their elemental analyses. However, these analyses did not provide any substantial structural elucidations.

The calculated elemental analyses for these polymers were based on polymerizations considered as resulting individually from fragments such as $RAr\overset{\ominus}{C}H-\overset{\oplus}{N}=N-$, $RArCH\colon$, and $RArC=N\cdot$, but

Downloaded At: 11:34 25 January 2011

none of the values derived matched the analytical values obtained. However, the found values were approximated if fragments of both the ionic and radical mechanisms were included in approximately equal molar quantities. The structures of the polymers from II and X appear to be more complex than those from III and IV, which were derived from the hydroxy-substituted azines. The spectra of the polymers from III and IV show bands in the region 1250 cm^{-1} attributable to the presence of an ether linkage, $-CH_2-O-C$. Thus part of these two polymers are composed of $-C_6H_4CH_2O-$ linkages, resulting most probably from the attack of the phenyldiazo ion or a phenyl carbene on a phenol. However, other segments, including nitrogen, are also present in these polymers.

The thermograms of the polymers from III and IV indicate a thermal stability higher than those from II and X, probably the result of a better defined polymer structure.

The monomeric azines were found in this study to undergo the aldehyde, amine, and bis exchange reactions similarly and parallel to the reactions of the Schiff bases previously reported [2-5, 11, 12]. However, the amine exchange between a Schiff base and hydrazine, Eq. (7), is not expected to be applicable to the preparation of high molecular weight polymers, since, at the temperatures used in these syntheses, the hydrazine will be lost, because it is the lowest-boiling component in the system. However, it may find application in the preparation of low molecular weight polymers by isolating the polymers without heating, such as by filtration from the reaction mixture. From the data obtained in this study on the decomposition of the monomeric azines, it is obvious that the polymerization reactions using multifunctional molecules must be performed at temperatures reasonably lower than the decomposition temperatures of the monomers as well as of the derived polymer, and also that the quantity of Lewis acid catalysts, if used, in the polymerizations must be restricted to small quantities, to avoid decompositions due to a decrease in the decomposition temperatures.

Downloaded At: 11:34 25 January 2011

REFERENCES

[1] G. F. D'Alelio and R. K. Schoenig, Polymeric Schiff Bases: The Syntheses and Thermal Stabilities of Polyazines and Derived Stilbenes, in preparation.

[2] G. F. D'Alelio, J. V. Crivello, R. K. Schoenig, and T. F. Huemmer, *J. Macromol. Sci.*, **A1**(7), 1161 (1967).

[3] G. F. D'Alelio, R. K. Schoenig, and J. V. Crivello, *J. Macromol. Sci.*, **A1**(7), 1299 (1967).

[4] G. F. D'Alelio, J. V. Crivello, R. K. Schoenig, and T. F. Huemmer, *J. Macromol. Sci.*, **A1**(7), 1321 (1967).

[5] G. F. D'Alelio, J. V. Crivello, T. R. Dehner, and R. K. Schoenig, *J. Macromol. Sci.*, **A1**(7), 1331 (1967).
[6] G. F. D'Alelio, W. F. Strazik, and T. F. Huemmer, *J. Macromol. Sci.*, **A2**(2), 335 (1968).
[7] T. Curtius and R. Jay, *J. Prakt. Chem.*, **39**, 45 (1889).
[8] G. Williams and A. S. C. Lawrence, *Proc. Roy. Soc. (London)*, **156A**, 44 (1936).
[9] H. Zimmerman and S. Somasekhara, *J. Am. Chem. Soc.*, **82**, 5865 (1960).
[10] G. F. D'Alelio, J. V. Crivello, R. K. Schoenig, and T. F. Huemmer, *J. Macromol. Sci.*, **A1**(7), 1251 (1967).
[11] G. F. D'Alelio, J. V. Crivello, T. Kurosaki, and R. K. Schoenig, *J. Macromol. Sci.*, **A1**(7), 1259 (1967).
[12] G. F. D'Alelio, T. Kurosaki, and R. K. Schoenig, *J. Macromol. Sci.*, **A1**(7), 1279 (1967).
[13] L. Ferguson and G. Branch, J. Am. Chem. Soc., **66**, 1468 (1944).
[14] B. Vörlander, *Ber.*, **39**, 810 (1906).
[15] *Handbook of Chemistry and Physics* (R. C. Weast, S. M. Selby, and C. D. Hodgman, eds.), 45th ed., Chemical Rubber Co., Cleveland, 1964.
[16] W. J. Pummer and L. A. Wall, *Natl. Bur. Std. (U.S.) Rep. 7782*, (1964).
[17] J. Burdon, *Tetrahedron*, **21**, 3373 (1965).
[18] L. A. Wall, W. J. Pummer, J. E. Fearn, and J. M. Antonucci, *J. Res. Natl. Bur. Std.*, **67A**, 481 (1963).
[19] J. Meisenheimer and F. Heim, *Ann.*, **335**, 274 (1907).
[20] P. Pascal and L. Normand, *Bull. Soc. Chim.*, **9**, 1029 (1911).
[21] L. B. Howard, G. E. Hilbert, R. Wiebe, and V. L. Gaddy, *J. Am. Chem. Soc.*, **54**, 3628 (1932).
[22] E. Freeman and B. Carroll, *J. Phys. Chem.*, **62**, 394 (1958).
[23] S. S. Hirsch, *J. Org. Chem.*, **32**, 2433 (1967).
[24] R. Busch, *Ber.*, **29**, 2143 (1896).
[25] W. M. Jackson and R. T. Conley, *J. Appl. Polymer Sci.*, **8**, 2163 (1966).

Accepted by editor October 28, 1967
Submitted for publication January 2, 1967

Downloaded At: 11:34 25 January 2011

Zusammenfassung

Die Zersetzungstempemperaturen zehn monomerer Azine, $RC_6H_4CH{=}N{-}N{=}HCC_6H_4R$, ist rein qualitativ von der elektronischen Struktur des Substituenten R abhängig. Eine Abhängigkeit ergab sich ebenfalls von den beitragenden Resonanzstrukturen und Wasserstoffbindungen, falls letztere in der Azingruppe auftreten. Die Ausbeuten an Stickstoff und Stilben sind nicht quantitativ und schwanken mit der Gruppe R. Die Zersetzungen ergaben sich als

Reaktionen erster Ordnung; beobachtete Abweichungen sind auf Nebenreaktionen zurückzuführen. Es wird angenommen, dass die Zersetzungsreaktion nicht ausschliesslich über einen ionischen Kettenreaktionsmechanismus vor sich geht, sondern dass auch Radikalprozesse beteiligt sind, wobei das relative Auftreten dieser Reaktionsarten mit R variiert. Die Zersetzung gewisser substitueirter monomerer Azine ergibt unlösliche, unschmelzbare Polymere.

Die monomeren Azine geben, ähnlich wie die monomeren Schiff'schen Basen, die Aldehyd-, Amin-, und Doppelaustauschreaktion bei Temperaturen, die unterhalt der Zersetzungstemperatur liegen.

Résumé

On a montré que les températures de la décomposition de dix azines monomères, $RC_6H_4CH{=}N{-}N{=}HCC_6H_4R$, sont qualitativement apparentées à la nature éléctronique du substituant R, à la résonance de structures et à la liaison hydrogène, si présente, dans la moitié azine. Les rendements d'azote et de stilbène ne sont pas quantitatifs et changent avec la nature de R. On a observé des cinétiques du premiér ordre pour les décompositions; les deviations paraissent résulter des réactions secondaires. On offre l'hypothese que la décomposition ne se produit pas exclusivement par une réaction ionique en chaine, mais aussi par un processus radicalaire libre, et que le taux de ces deux procedés varie avec R. La décomposition de quelques azines monomères substitués donnent des polymères insolubles, infusibles.

Les azines monomères, d'une maniére analogue aux bases monomères de Schiff, subissent les aldehydo-, amino-, et les réactions de bis-échange, à des températures plus bases que la décomposition.

Downloaded At: 11:34 25 January 2011