KINETIC STUDY OF THE TRIFLUOROACETONITRILE–BUTADIENE CYCLIZATION[1]

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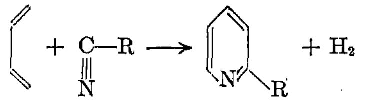
A kinetic study of the trifluoroacetonitrile–butadiene cyclization reaction in the temperature range 350–520° is reported. The reaction is homogeneous and second order, the rate expression being $k_2 = 2.1 \times 10^9 e^{-21,500/RT}$. Comparison of these data with the kinetic parameters of normal diene reactions, at high temperatures, shows that this reaction is an example of a Diels–Alder process in which the dihydro-cyclic adduct loses hydrogen spontaneously under the conditions of the reaction to form 2-trifluoromethylpyridine. From consideration of the entropies of activation, it follows that the transition state, while similar to that in the normal Diels–Alder process, may be more bonded in structure.

The reaction of cyanogen and related nitriles with 1,3-dienes to form 2-substituted pyridines; *i.e.*



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has been studied by Janz and co-workers[2] in the homogeneous gas phase and over catalyst surfaces. More recently it was observed[3] that with trifluoroacetonitrile and butadiene, reaction proceeds readily without the presence of catalysts at 400° with the formation of 2-trifluoromethylpyridine as product. The present communication describes a kinetic study of this reaction in the temperature range 350–520°. A discussion of the results in the light of the high temperature Diels–Alder and the cyanogen–butadiene reactions gives a further insight on the mechanism of this generalized cyclization–dehydrogenation reaction.

Experimental

Description of Flow Apparatus.—The system used was an all glass apparatus, having a preheater maintained at about 250° so that the gases entering the reaction zone were of sufficiently high temperature to prevent any cooling at the entrance. The gas flows were controlled by two needle valves (Edwards and Co.) and read on rotameters (Emil Greiner) which had been calibrated previously for both trifluoroacetonitrile and butadiene. The nitrogen flow was measured by a capillary type flowmeter. The temperature in the reaction zone was measured by means of six chromel-alumel thermocouples placed in a well over the length of the reactor.

The trifluoroacetonitrile (Columbia Organic) and butadiene (Matheson) were transferred from the cylinders supplied by the manufacturers to glass cylinders and were degassed on a vacuum system. The glass cylinder of butadiene was placed in an ice–water mixture previous to the commencement of a run and the trifluoroacetonitrile cylinder in an acetone–chloroform mixture to which Dry Ice was added until the temperature was constant in the range −62 to −58°.

The product and the unreacted reactants were collected in two Dry Ice traps and two liquid nitrogen traps. The system was flushed for 30 minutes with nitrogen before and after each experiment. It was found that all the product was collected in the first Dry Ice trap in addition to most of the butadiene. These were subsequently separated by a simple distillation. The trifluoroacetonitrile was collected as a white solid in the liquid nitrogen traps. A summary of experiments completed is given in Table I. From a consideration of the limits of error in the operation of flow methods, a variation of 10% is possible in the rate constant. However, for internal consistency the values given in Table I are shown with more significant figures than are necessary. An experiment designed to correlate the amount of hydrogen evolved with the pyridinic product formed (runs 37 and 39) utilized a Toepler pump and a calibrated volume to collect this gas. The number of moles of hydrogen was calculated from the pressure and volume of the gas thus collected escaping from the liquid nitrogen traps in the reaction system.

Determination of 2-Trifluoromethylpyridine for Rate Calculations.—In the initial stage of this work, it was thought the refractive index would afford a means of determining the amount of trifluoromethylpyridine present in the product. It was found that this method gave unsatisfactory results, probably because the other substances present interfere with the refractive index determination, which was based on a calibration assuming only trifluoromethylpyridine and vinylcyclohexene as products.

The ultraviolet spectra of 2-trifluoromethylpyridine and 3-vinylcyclohexene-1 were examined in order to find out if trifluoromethylpyridine could be determined in the presence of vinylcyclohexene and the other products formed. The spectrum of trifluoromethylpyridine in alcohol is shown in Fig. 1. Two maxima were observed close together at 251 and 256 mμ and having extinction coefficients of 1685 and 1784, respectively. The spectrum of vinylcyclohexene in alcohol in the same region showed a peak at 273 mμ and ε 4.5. The values obtained for the extinction coefficient over the range 220–340 mμ did not exceed 8, while in the region 250–260 mμ the extinction coefficient had the value of about 4. From this it is apparent that the interference in the spectrum of trifluoromethylpyridine caused by the presence of vinylcyclohexene is exceedingly small and may be considered negligible in the use of ultraviolet analysis for the quantitative determination of the trifluoromethylpyridine.

A distillation of the reaction product was carried out to separate the fraction boiling higher than trifluoromethylpyridine. A study of the ultraviolet spectrum showed that the higher boilers did not interfere with the determination of trifluoromethylpyridine. It follows that this method for the determination of trifluoromethylpyridine in the presence of vinylcyclohexene and the high boilers is satisfactory.

Results and Discussion

The forms of the kinetic rate equations in flow systems have been considered by Harris[4] in detail. For a second-order process, where the limiting cases of complete and negligible diffusion can be neglected; *i.e.*, for low conversions, the rate law has the form

$$k_2 = \frac{V_1^2}{V_r}\left(\frac{N_C}{N_{A_1}N_{B_1}}\right) \text{ cc. mole}^{-1} \text{ sec.}^{-1} \qquad (2)$$

in which V_1 is the volume of the gases entering the reaction zone, V_r, at the temperature and pressure of the reaction, and N_{A_1}, N_{B_1}, N_C are the moles of trifluoroacetonitrile, butadiene and trifluoromethylpyridine per second flowing through the reaction

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[1] Part XI in the series, "The Reaction of Cyanogen and Related Nitriles with 1,3-Dienes." Presented before the General Session, Petroleum Division, American Chemical Society, Atlantic City, September, 1956.

[2] G. J. Janz and co-workers, *J. Am. Chem. Soc.*, **76**, 6377 (1954); **77**, 3014 (1955).

[3] J. M. S. Jarvie, W. E. Fitzgerald, and G. J. Janz, *ibid.*, **78**, 978 (1956).

[4] G. M. Harris, THIS JOURNAL, **51**, 505 (1947).

TABLE I

RUN DATA FOR BUTADIENE–TRIFLUOROACETONITRILE REACTION

Run	Partial pressure of reactants (atm.)			Contact time (sec.)	Conversion × 10², %		Temp., °K.	Rate constant, cc. moles^{-1} sec.$^{-1}$
	CF_3CN	C_4H_6	N_2		CF_3CN	C_4H_9		
5	0.383	0.413	0.205	39.3	6.45	5.98	666	219
6	.367	.292	.402	29.6	3.79	3.98	678	243
7	.254	.253	.492	23.4	1.63	1.64	687	156
12	.478	.522	...	41.1	9.82	10.33	672	252
13	.387	.400	.213	37.8	15.32	14.80	718	596
14	.371	.327	.302	31.5	5.27	5.98	688	289
15	.406	.384	.210	37.0	17.01	18.00	722	708
16	.396	.390	.215	35.2	44.43	45.10	776	2060
17	.407	.389	.205	35.5	18.22	19.08	733	795
18	.377	.396	.227	41.0	12.49	11.90	703	444
19	.402	.386	.212	38.9	7.85	8.18	694	298
20	.254	.260	.486	26.1	2.21	2.17	672	179
21	.198	.190	.612	19.0	0.567	0.592	674	87.1
22	.354	.354	.292	35.5	4.38	4.37	668	191
23	.442	.558	...	38.0	10.13	8.01	683	268
24	.399	.503	.098	40.6	7.10	5.64	671	192
25	.408	.498	.094	36.6	22.42	18.36	715	721
26	.551	.449	...	36.6	20.89	25.66	726	757
27	.574	.426	...	37.5	24.31	32.74	749	934
28	.618	.382	...	30.1	35.71	57.80	796	2030
29	.597	.403	...	38.5	10.13	15.01	696	373
30	.588	.412	...	43.5	1.95	2.79	630	56.3
31	.422	.356	.216	12.1	0.121	0.148	675	16.1
32(P)[a]	.613	.388	...	47.1	9.48	14.99	688	293
33(P)[a]	.484	.296	.220	36.3	4.98	8.14	688	261
37	.595	.405	...	39.7	10.90	16.00	696	387 (402)[b]
39	.475	.525	...	39.6	14.00	12.69	693	383 (386)[b]

[a] (P) Reactor packed with Pyrex chips. [b] ( ) In Rate Constant column refers to k_2 calculated from moles of hydrogen evolved.

zone. In the present case, this relation can be expressed by the equation

$$k_2 = \frac{\text{(fractional conversion of } CF_3CN)}{\text{(contact time)(partial pressure of } C_4H_6)} \quad (3)$$

for convenience of calculation. The rate constants, k_2, reported in Table I were computed in this manner.

Kinetic Results

The effects of contact time, partial pressures and surface area were investigated to test the validity of the rate equation, and the order of the reaction. The dependence of the rate constant on the contact time was investigated at 400°. The data (runs 5, 6, 7, 12, 20, 21, 23, 24 and 31, Table I) were extrapolated to this exact temperature using the slope of the Arrhenius plot. It was found that at contact times greater than 30 sec., the rate constant was independent of time. The failure of the rate law at contact times less than 30 sec. is not understood, but may be, in part, due to the fact that temperature equilibrium may not be attained by the gases. In the present work, the contact times used at all temperatures were greater than 30 sec.

The rate constants, normalized to 420°, for the variation in partial pressures with nitrogen gas (runs 6, 13, 18, 22 and 24, Table I) and in the molar ratios of reactants (runs 6, 13, 22, 24, 26 and 29, Table I) were constant (338 ± 18) within the experimental limits of error. The homogeneity of this reaction was established using a reaction vessel packed with Pyrex chips to increase the surface area fiftyfold (runs 32 and 33).

The temperature dependence of the rate constant was investigated to obtain the parameters of the Arrhenius equation. The plot of log k_2 and $1/T$°K. is linear over the whole range investigated. The rate equation for this process,

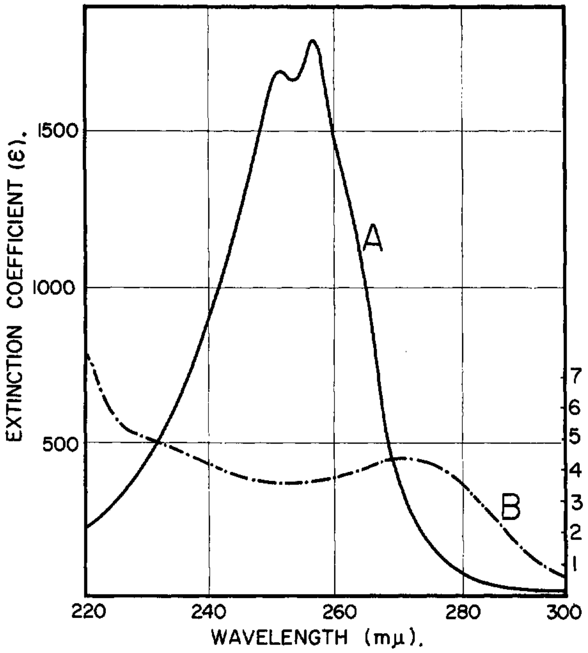


Fig. 1.—Ultraviolet absorption spectra of trifluoromethylpyridine and 3-vinylcyclohexene-1 in alcohol: A, trifluoromethylpyridine; B, 3-vinylcyclohexene-1.

accordingly, is

$$k_2 = 2.1 \times 10^9\, e^{-21{,}500/RT} \qquad (4)$$

the reaction being second order over-all, but first order with respect to each of the reactants, butadiene and trifluoroacetonitrile, respectively. The rate constants, interpolated at even temperatures, are given in Table II.

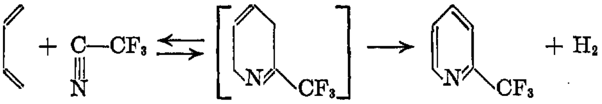
TABLE II

RATE CONSTANTS[a] FOR THE TRIFLUOROACETONITRILE–BUTADIENE REACTION OVER THE TEMPERATURE RANGE 350–520°

Temp., °C.	k_2, cc. moles^{-1} sec.$^{-1}$	Temp., °C.	k_2, cc. moles^{-1} sec.$^{-}$
350	58.1	440	528
360	76.6	450	649
370	101	460	802
380	131	470	982
390	169	480	1190
400	210	490	1430
410	274	500	1720
420	345	510	2070
430	429	520	2470

[a] Interpolated from the experimental results plotted as log k_2 against $1/T$°K.

The reaction of trifluoroacetonitrile with butadiene may be formulated as



in which the dihydropyridine derivative postulated above corresponds to the normal adduct in an orthodox Diels–Alder association reaction. Theoretical considerations[5] on the stability of dihydropyridine relative to pyridine show that the dihydro compound is thermodynamically quite unstable, and thus, if formed under conditions favoring aromatization, would be expected to pass over to the pyridinic product. A hydrogen–pyridinic product balance in the ratio of 1.0/1.0 accordingly is predicted for the over-all process under consideration. In the present work an experiment was devised in which the amount of hydrogen evolved during the reaction could be collected. The results (runs 37, 39, Table I, 4.64 × 10^{-2}, 4.46 × 10^{-2}, and run 39, 3.40 × 10^{-2}, 3.75 × 10^{-2} moles of hydrogen and trifluoromethylpyridine, respectively) confirmed the prediction above; *i.e.*, that hydrogen is produced in the same molar ratio as the pyridinic product.

An insight on the mechanism of this reaction can be gained by comparison of the kinetic results with other high temperature homogeneous gas phase reactions. A summary of the pertinent data is given below.

Diene	Dienophile	Temp. range (°C.)	*A* Factor	Δ*E*	Δ*S**	Ref.
Butadiene	Acrolein	155–322	1.46 × 10^9	19.7		6
Butadiene	Crotonaldehyde	242–300	0.9 × 10^9	22.0		7
Butadiene	Butadiene	173–386	9.2 × 10^9	23.69	−16.9	8
		418–650	1.4 × 10^{11}	26.8		9
Butadiene	Ethylene	487–648	3.0 × 10^{17}	27.5	−14.5	9
Butadiene	Cyanogen	325–450	1.6 × 10^{12}	31.6	−11.8	10
Butadiene	Trifluoroacetonitrile	357–523	2.1 × 10^9	21.5	−19.4	This work

The entropies of activation, Δ*S**, have been calculated from the absolute rate theory equations[11] for two typical Diels–Alder type reactions as well as for the trifluoromethylpyridine and cyanogen cyclizations. The Arrhenius *A* factor and the energy of activation for the trifluoroacetonitrile–butadiene reaction fall within the range (10^9–10^{10}, 20–24 kcal.) for typical Diels–Alder association reactions. It follows from this that the kinetic parameters of the present system may be attributed to a rate-controlling step similar to that for the Diels–Alder addition, *i.e.*, the cyclization step. The kinetics of the diene associations at high temperatures in the homogeneous gas phase have been discussed recently in detail.[9] It was shown that a cyclic transition complex was in best accord with all available rate data. The entropy of activation in the trifluoroacetonitrile–butadiene cyclization is about 2 to 4 e.u. more negative than that in the orthodox Diels–Alder associations. If significant, this indicates that the transition complex has a more bonded structure in this cyclization than in the comparable diene associations.

It is of interest to compare the kinetic results reported for the cyclization of cyanogen with butadiene[10] with the present work. The energy of activation for the former is 5 to 10 kcal./mole higher, and the frequency factor 10^2 higher than that obtained for the trifluoroacetonitrile–butadiene cyclization, and the orthodox Diels–Alder reactions. The entropy of activation calculated for the cyanogen–butadiene reaction (−11.8 e.u.) is considerably greater than the values found for the present system and the related diene associations. A comparison of the rotational entropy increments accompanying the configurational changes when butadiene and cyanogen approach the position for 1,4-addition (−6 e.u.), with the loss in translational entropy in the formation of a bonded cyclic complex (−40 e.u.), indicates that the transition complex must have greater looseness than in the other reactions. The orientation of butadiene and cyanogen into the position for 1,4-addition accounts for approximately one half of the entropy of activation, so that the degree of bond formation in the transition complex must be quite incipient.

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The use of trifluoroacetonitrile in the dienes-nitriles cyclization has also been of interest since the (CN) group is coupled with a group having a very strongly electrophilic nature. Of the nitriles previously studied (HCN, CH_3CN, C_2H_5CN, C_6H_5CN, $CH_2{=}CH{-}CN$ and $(CN)_2$) only cyanogen reacted at an appreciable rate in the homogeneous gas phase. In the present instance, the high reactivity of the (CN) group in trifluoroacetonitrile may be attributed to the polarization of the dienophilic link by the proximity of the CF_3 group with its strong electrophilic properties. A study of importance of this effect in the mechanism in the homogeneous gas phase reaction is in progress.

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A STUDY OF THE CONDUCTANCE BEHAVIOR OF SOME UNI-UNIVALENT ELECTROLYTES IN DIMETHYL SULFOXIDE AT 25°[1]

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The conductances of nineteen uni-univalent electrolytes in dimethyl sulfoxide have been measured at 25° for solute concentrations ranging from 3–700 × 10^{-5} *N*. In every case, excellent agreement exists between the experimentally observed behavior and that predicted theoretically by the Onsager equation. The limiting equivalent conductance of each electrolyte has been evaluated by an extrapolation of a Shedlovsky plot of Λ'_0 *versus* C. Limiting ionic equivalent conductances which are based upon the equal conductances of the *n*-octadecyltrimethylammonium and the *n*-octadecyl sulfate ions agree within 2–5% with those which are based upon an assumed constancy of the limiting conductance–viscosity product of the tetra-*n*-butylammonium ion in non-aqueous solvents. The conductance behavior of electrolytes in dimethyl sulfoxide closely resembles that for the same electrolytes in dimethylformamide and in pyridine.

Introduction

Dimethyl sulfoxide (CH_3SOCH_3) is a recently introduced, versatile solvent which now has become available commercially as a relatively inexpensive, very pure product. It is characterized by a broad, convenient liquid range (18.4–189°), a moderate viscosity (0.0196 poise), a relatively high dielectric constant (46.6), and extensive dissolving power. Its high Trouton constant (29.5)[2] is evidence that it is an associated liquid. The structural aspects of dimethyl sulfoxide indicate that it should function as an electron-donor solvent; hence, its solutions might be expected to exhibit solute-solvent interactions similar to those which have been observed for solutions of the same solutes in dimethylformamide, acetone or pyridine. The objectives of this research, therefore, have been to investigate the potentialities of dimethyl sulfoxide as an electrolytic solvent through a study of the conductimetric behavior of several electrolytes and to compare the pattern of results for dimethyl sulfoxide solutions with those which have been reported for solutions of the same electrolytes in other electron-donor solvents.

Experimental

1. **Purification of Solvent.**—Dimethyl sulfoxide, which was supplied as 99.9% pure by the Stepan Chemical Company, was refluxed for several hours in contact with calcium oxide and then was fractionated through an efficient distillation column at a reduced pressure of approximately 5 mm. The middle fractions thus obtained were fractionated one or more times at the same pressure until the dimethyl sulfoxide which finally was retained had a conductivity which did not exceed 3 × 10^{-8} ohm^{-1} cm.$^{-1}$ as well as the desired density, viscosity and dielectric constant.

2. **Purification of Salts.**—Tetra-*n*-butylammonium and trimethylphenylammonium iodides and sodium benzenesulfonate (all Eastman Kodak Co. grade) were recrystallized three times from methanol or ethanol–ether mixtures. Trimethylphenylammonium benzenesulfonate (practical grade) was treated with boneblack prior to several recrystallizations from methanol. These salts were dried to constant weight *in vacuo* at 70°.

The purification and the drying of the potassium and sodium salts have been described in previous papers.[3,4]

The following salts were furnished in purified form by E. D. Wilhoit[5]: potassium *n*-octadecyl sulfate, m.p. 179–181°; *n*-octadecyltrimethylammonium nitrate, m.p. 200–202°; *n*-octadecyltrimethylammonium iodide, m.p. 234–236°.

3. **Apparatus and Procedure.**—The bridge, cells, bath and temperature control and procedure of the conductance measurements have been described previously.[3,6] The dielectric constant of each fraction of dimethyl sulfoxide was determined at ten megacycles using the equipment and procedure which have been described by Leader.[7] The viscosity of each fraction of dimethyl sulfoxide was measured using size-50 Cannon–Fenske viscometers which were calibrated by the Cannon Instrument Company. Kinetic energy corrections were assumed to be negligible.

The following data for dimethyl sulfoxide at 25° were used in the calculations: density, 1.096 g./ml.; viscosity, 0.0196 poise; dielectric constant, 46.6. Values of the fundamental constants were taken from a 1952 report of the Subcommittee on Fundamental Constants.[8]

Results

Corresponding values of the equivalent conductance, Λ, and the concentration in gram equivalents per liter, C, are presented in Table I for each of the

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(1) Taken from a thesis submitted by George R. Lester in partial fulfillment of the requirements for the degree of Master of Science.

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