TABLE I

MONOMERIC KETENES

Phenoxyketene monomers	M. p., °C.	Yield,[a] %	Formula	Analyses: Mol. wt.[b] Calcd.	Mol. wt.[b] Found	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
Phenoxy	92–93	31.5	$C_8H_6O_2$	134.1	140.5	71.66	70.76	4.51	4.05
2-Chloro	135–136	55.2	$C_8H_5O_2Cl$	168.5	173.1	57.01	57.03	2.97	2.42
	B. p. 110–115 (1 mm.)								
4-Chloro	141–142	77.5	$C_8H_5O_2Cl$	168.5	170.4	57.01	56.85	2.97	2.54
2,4-Dichloro	125–126	43.8	$C_8H_4O_2Cl_2$	203.0	224.0	47.33	48.05	1.97	1.54
2,4,5-Trichloro	146–147	41.7	$C_8H_3O_2Cl_3$	237.5	237.4	40.46	39.84	1.26	1.14
2,4,6-Trichloro	178–179	56.4	$C_8H_3O_2Cl_3$	237.5	245.0	40.46	40.08	1.26	1.39

[a] Based on the amount of unreacted acid chloride. [b] Molecular weights determined cryoscopically: Meldrum, Saxer and Jones, THIS JOURNAL, **65**, 2023 (1943).

TABLE II

PHENYLHYDRAZIDES OF MONOMERIC KETENES

Hydrazides, phenoxyketenes	Yield, %	M. p., °C.	Formula	Nitrogen, %[a] Calcd.	Nitrogen, %[a] Found
Phenoxy	20	97–98	$C_{14}H_{14}O_2N_2$	11.56	11.63
2-Chloro-	40	94–95	$C_{14}H_{13}O_2N_2Cl$	10.13	10.61
4-Chloro-	40	118–119 dec.	$C_{14}H_{13}O_2N_2Cl$	10.13	10.33
2,4-Dichloro-	38	112–113	$C_{14}H_{12}O_2N_2Cl_2$	9.00	[b]
2,4,5-Trichloro-	14	203–204	$C_{14}H_{11}O_2N_2Cl_3$	8.10	7.97
2,4,6-Trichloro-	55	135–135.5	$C_{14}H_{11}O_2N_2Cl_3$	8.10	8.24

[a] Determined by semi-micro Dumas method. [b] Compound decomposed upon prolonged drying.

TABLE III

AMIDES AND ANILIDES OF PHENOXYKETENES

Phenoxyketenes	Amides: Yield, %	M. p., °C.	Formula	Nitrogen, %[a] Calcd.	Nitrogen, %[a] Found	Anilides: Yield, %	M. p., °C.	Formula	Nitrogen, % Calcd.	Nitrogen, % Found
Phenoxy	75	184–185	$C_8H_9O_2N$	9.27	9.35	40	103–104	$C_{22}H_{19}O_4N$	3.90[g]	4.15
2-Chloro-	73	179–180[b,3]	$C_8H_8O_2NCl$	7.55	7.52	65	121–122[e,3]	$C_{14}H_{12}O_2NCl$	5.35	5.69
4-Chloro-	73	197–198[c,3]	$C_8H_8O_2NCl$	7.55	7.50	52	120–121[f,3]	$C_{14}H_{12}O_2NCl$	5.35	5.40
2,4-Dichloro-	55	176–178	$C_8H_7O_2NCl_2$	6.40	6.48	60	116–117	$C_{14}H_{11}O_2NCl_2$	4.73	4.15
2,4,5-Trichloro-	56	174–175	$C_8H_6O_2NCl_3$	5.51	6.23	61	141–141.5	$C_{14}H_{10}O_2NCl_3$	4.24	4.46
2,4,6-Trichloro-	75	184–185	$C_{16}H_9O_4NCl_6$	2.90[d]	3.11	39	134–135	$C_{14}H_{10}O_2NCl_3$	4.24	4.00

[a] Analyzed by semi-micro Dumas method. [b,c,e,f] Minton and Stephens prepared these compounds from the acid chlorides and reported 149–155°; 133°; 121°; 125°, respectively. [d,g] Calculated on basis of dimeric ketene.

Experimental

The dehydrohalogenation procedure used was similar to that reported by Sauer.[2] A small excess of triethylamine over acid chloride was employed in each experiment. Each monomer was purified by recrystallization from a suitable solvent. The ketene monomers were white crystalline solids which were highly hygroscopic. This fact made it exceedingly difficult to obtain dry samples for analysis.

A quantity of unreacted acid chloride was recovered from each preparation.

Analytical data and several physical constants of the six ketene monomers are shown in Table I.

All melting points in this paper are uncorrected.

Phenylhydrazides.—To a solution of the ketene (0.5 g.) in 25 ml. of anhydrous diethyl ether was added 2 ml. of phenylhydrazine. The hydrazide precipitated immediately as white crystals which were then filtered and recrystallized from dilute ethanol. Upon drying the hydrazides turned slightly brown.

Attempts were made to prepare the *p*-nitrophenyl and 3,5-dinitrophenylhydrazides. In each case the product formed as yellow crystals which decomposed rapidly upon isolation and drying.

Properties and analytical data of the phenylhydrazides are shown in Table II.

Amides.—A 0.5-g. sample of each ketene monomer was dissolved in diethyl ether, and dry ammonia gas passed into the solution until precipitation was complete. The crude amide was filtered and recrystallized from benzene. The pure amides were white crystalline solids.

Anilides.—A 0.5-g. sample of each ketene was dissolved in 25 ml. of anhydrous ether and 2 ml. of aniline was added. The mixture was then refluxed for five minutes. On cooling the anilide crystallized out and was filtered. Recrystallization was made from dilute ethanol.

Analytical data and physical constants for the amides and anilides are given in Table III.

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[2] Sauer, THIS JOURNAL, **69**, 2444 (1949).

[3] Minton and Stephens, *J. Chem. Soc.*, **121**, 1598 (1922).

The Specific Rotation of Yeast Adenylic Acid in Anhydrous Formamide[1]

BY DAVID LIPKIN AND GEORGE C. MCELHENY

In connection with work in progress in this Laboratory on the chemistry of the nucleic acids, it became necessary to prepare considerable quantities of pure adenosine-3′-phosphoric acid. Several lots of commercial yeast adenylic acid were obtained[2] and purified by recrystallization of the brucine salt.[3] The yields of brucine

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[1] This research was supported in part by Contract No. AT-29-1-GEN-77 between the United States Atomic Energy Commission and Washington University.

[2] Schwarz Laboratories, Inc., Mount Vernon, N. Y.

[3] Jones and Kennedy, *J. Pharmacol. Exp. Therap.*, **13**, 45 (1919); Levene, *J. Biol. Chem.*, **40**, 415 (1919); Thannhauser, *Z. physiol. Chem.*, **107**, 157 (1919).

adenylate obtained from the several samples of yeast adenylic acid by precipitation under standard conditions varied rather markedly. This was surprising in view of the fact that the nitrogen and phosphorus analyses of the samples, as well as their specific rotations in 10% hydrochloric acid, were in good agreement with the values for yeast adenylic acid.[4] Furthermore, the specific rotation in 10% hydrochloric acid did not vary appreciably from one lot of acid to another.

In an attempt to correlate this variation in yield of brucine adenylate with the purity of the various samples, two other tests were carried out on several commercial samples of yeast adenylic acid as well as on three samples of purified acid. One of these was a measurement of the decomposition temperature,[5] while the other was a determination of the specific rotation in anhydrous formamide solution. Since the rate of solution of yeast adenylic acid in formamide of low conductivity is slow, further measurements of the specific rotation were made in anhydrous formamide containing small amounts of N-methylmorpholine.

The results obtained with various samples of yeast adenylic acid are summarized in Table I. Although the specific rotations of the two commercial samples in 10% hydrochloric acid are not appreciably different,[6] the specific rotations of these samples do differ considerably in either relatively impure formamide (specific conductance 10^{-3} ohms^{-1} cm.$^{-1}$) or in pure formamide (specific conductance 5×10^{-5} ohms^{-1} cm.$^{-1}$) containing 2% anhydrous N-methylmorpholine. The specific rotation of purified yeast adenylic acid in formamide solution (see samples 3, 4 and 5) is different, furthermore, from that of the commercial samples.

TABLE I[a]

Sample no.	1[b]	2[b]	3[c]	4[d]	5[e]
Dec. temp., °C.	177	181	185	186	184
Yield of brucine adenylate, %	32	52	...	...	...
$[\alpha]^{29}\text{D}$ in 10% HCl[f]	−35.9°	−35.3°	...	−38.0°	−38.0°
$[\alpha]_\text{D}$ in formamide ($L = 10^{-3}$ ohms^{-1} cm.$^{-1}$)[g,h]	−75.0°	−66.4°	−61.1°	−60.8°	−63.8°
$[\alpha]^{27.5}\text{D}$ in formamide ($L = 5 \times 10^{-5}$ ohms^{-1} cm.$^{-1}$) containing 2 vol. % anhydrous N-methylmorpholine[i]	−73.8°[j]	−66.9°	−55.1°	...	−59.0°

[a] All specific rotations are calculated on an anhydrous basis. [b] Two different samples of commercial yeast adenylic. [c] Yeast adenylic acid recovered from recrystallized brucine adenylate (m. p. 172°, cor.) by precipitation with hydrochloric acid. The brucine adenylate was prepared from sample no. 1. [d] Sample 3 recrystallized from hot water. [e] Sample 4 recrystallized from hot water. The reason for the drop in decomposition temperature and change in $[\alpha]_\text{D}$ in formamide on recrystallization is not understood. [f] *c*, 1.92. [g] *c*, 0.53. [h] The temperature at which these specific rotations were measured varied between 25–29°. [i] *c*, 0.46. Doubling the concentration of adenylic acid did not change the value of the specific rotation. [j] The same value was obtained in a formamide solution containing 1 vol. % N-methylmorpholine.

It appears that the specific rotation of yeast adenylic acid in anhydrous formamide[7] is a more sensitive criterion of purity for this substance than the decomposition temperature, percentage of nitrogen and phosphorus, or the specific rotation in 10% hydrochloric acid. The impurity which is present in samples 1 and 2 is not known. It must contain, however, approximately the same percentage of nitrogen and phosphorus as adenosine-3′-phosphoric acid. One possible explanation of the data[8] is that the "impurity" is an isomeric adenosinephosphoric acid.[9] In order to determine whether this is a plausible explanation, measurements of the specific rotation and decomposition temperature were made on samples[10] of adenosinephosphoric acids which had been carefully purified by ion exchange techniques.[9] The results obtained on these samples, including determinations of the water of crystallization, are summarized in Table II.

TABLE II

Sample	Dec.[a] temp., °C.	$[\alpha]^{25}\text{D}$[b]	H_2O,[c] %
Adenosine-3′-phosphoric acid	191	−58.7°	5.24
Adenosine-5′-phosphoric acid	178	−50.0°	5.63
Adenosinephosphoric acid of Carter and Cohn[9]	183	−84.3°	7.37

[a] 1:1 mixtures of Carter and Cohn's adenosinephosphoric acid with either adenosine-3′- or -5′-phosphoric acid showed a depression of the decomposition temperature. [b] All specific rotations are calculated on an anhydrous basis. These rotations were measured in anhydrous formamide ($L = 7 \times 10^{-5}$ ohms^{-1} cm.$^{-1}$) containing 2 vol. % anhydrous N-methylmorpholine; *c*, 0.5. [c] The value calculated for $C_{10}H_{14}O_7N_5P \cdot H_2O$ = 4.93% H_2O; for $C_{10}H_{14}O_7N_5P \cdot 1.5\ H_2O$ = 7.22% H_2O.

Using the yield of brucine adenylate as a measure of the percentage of adenosine-3′-phosphoric acid present in commercial yeast adenylic acid and the specific rotations of the pure isomeric adenosinephosphoric acids (Table II), specific rotations were calculated for samples 1 and 2 (Table I). These calculated values are in good agreement with the observed values, indicating that the principal "impurity" present

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(4) Berlin and Westerberg, *Z. physiol. Chem.*, **281**, 98 (1944); Embden and Schmidt, *ibid.*, **181**, 135 (1929); Levene and Bass, "Nucleic Acids," The Chemical Catalog Company, New York, 1931.

(5) An aluminum melting point block was used in making these measurements. The sealed capillary tube containing the sample was introduced into the block at 155° and the block heated at the rate of 8° per minute. The decomposition temperature was taken as the temperature at which gas evolution occurred. All decomposition temperatures are corrected.

(6) Another commercial sample of yeast adenylic acid which gave a 70% yield of brucine adenylate had the same $[\alpha]_\text{D}$ in 10% HCl as sample no. 1.

(7) Anhydrous formamide is also being examined as a reaction medium for the tritylation of adenosine-3′-phosphoric acid.

(8) Sample 1 gave a negative Fehling test and also was shown to contain only a trace of inorganic phosphate. The impurities could not, therefore, have been either the adenine salt of ribosephosphoric acid or the adenosine salt of phosphoric acid.

(9) Carter and Cohn, *Federation Proceedings*, **8**, 190 (1949); Cohn, THIS JOURNAL, **71**, 2275 (1949).

(10) We wish to thank Dr. Charles E. Carter of the Oak Ridge National Laboratory for supplying us with these samples.

in some commercial samples of yeast adenylic acid may be the new adenosinephosphoric acid isomer of Carter and Cohn.[9]

Experimental

Formamide was purified by distillation from calcium oxide at a pressure of 1–3 mm., using a still similar to that described by Hickman.[11] The distillate was redistilled from calcium oxide. Dry nitrogen was then bubbled through this second distillate for several hours. The best formamide obtained by this procedure had a specific conductance of 4×10^{-5} ohms^{-1} cm.$^{-1}$.[12,13]

N-Methylmorpholine (Carbide and Carbon Chemicals Corp.) was dried over solid potassium hydroxide and then fractionally distilled from barium oxide.

Rotations were measured either with a Schmidt and Haensch or a Rudolph No. 80 polarimeter.

The water content of the various samples was determined[14] by means of the apparatus of Milner and Sherman.[15] The samples were dried *in vacuo* at 110° using Drierite as the desiccant.

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(11) Hickman, *Chem. Revs.*, **34**, 55 (1944).

(12) Verhoek, This Journal, **58**, 2577 (1936), reports a specific conductance of about 5×10^{-5} ohms^{-1} cm.$^{-1}$ for formamide purified by his distillation procedure.

(13) We wish to thank Mr. Jonathan S. Dixon for preparing the samples of formamide used in this work.

(14) We wish to thank Miss Dorothy Kuenne for these analyses.

(15) Milner and Sherman, *Ind. Eng. Chem., Anal. Ed.*, **8**, 427 (1936).

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Emulsion Copolymerization of Butadiene and Styrene at Low Temperatures[1]

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The present work was undertaken in order to develop, if possible, a method for the copolymerization of butadiene and styrene which would be successful at −20°. The recipe in Table I, although not particularly rapid, occasionally gave soluble polymers of high intrinsic viscosity. The polymerizations, however, were not at all reproducible and many identically charged runs gave results ranging all the way from no polymer whatever to polymers with intrinsic viscosities as high as 5. It was suspected that atmospheric oxygen was responsible for this non-reproducibility of results, and every effort was taken to remove all air from the system before polymerization was started. Air was removed by adding excess butadiene and allowing it to evaporate; it was swept out mechanically with nitrogen; and it was removed along with excess butadiene from the closed system by means of a hypodermic needle inserted through self-sealing polymerization bottle caps. Even with these precautions the results were still quite erratic.

Table I

−20° Polymerization Recipe

Water	20.0 g.
Glycerol	20.0
$Na_4P_2O_7 \cdot 10H_2O$	0.25
$Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$	0.25
Potassium oleate	1.0
Benzoyl peroxide	0.1
Styrene	5.0
Butadiene	15.0

It, therefore, seemed possible that oxygen had already done its damage before all air was removed from the system and such actually proved to be the case. When the *entire* charging technique was carried out under nitrogen this recipe at −20° gave reproducible conversions of soluble copolymers with intrinsic viscosities of between 4.00 and 5.00. It is significant that benzene soluble polymers were obtained even though no modifier was added to the recipe. When the above charging technique was used for polymerization at 0°, 85% conversions were obtained in nine hours. This work is further confirmation of the observation of Hobson and D'Ianni[2] that removal of oxygen from other oxidation–reduction polymerization recipes at 41°F. results in faster polymerizations than are obtained in the presence of oxygen.

Experimental

Polymerization at −20°.—A solution of 2.5 g. of finely pulverized sodium pyrophosphate decahydrate in 105 ml. of redistilled water was prepared. This solution was poured directly into a clean 28-oz. ginger ale bottle which had previously been flushed out with nitrogen and placed on a steam cone. Nitrogen was kept streaming into the bottle during all the charging period until after the addition of butadiene. Then 2.5 g. of pulverized ferrous ammonium sulfate hexahydrate dissolved in 35 ml. of redistilled water was added through a funnel to the bottle. A cloudy precipitate formed in the solution, which was heated slowly with hand agitation to about 60°. Meanwhile, 10 g. of dry potassium oleate (*p*H 10) was dissolved in 60 ml. of redistilled water with slight warming if necessary and then 200 g. of glycerol was added with stirring to the soap solution. When the activator solution had come to temperature, the soap–water–glycerol solution was added to it and the bottle, after preliminary cooling under the water-tap, was placed in an ice–salt-bath. (The flow of nitrogen into the bottle was maintained.) After the temperature of the contents had reached 0°, 50 ml. of styrene containing 1.0 g. of benzoyl peroxide was added, and then about 175 g. (an excess) of butadiene. The excess butadiene was evaporated to proper weight (150 g. of butadiene), the bottle was crimp-capped, and the contents were allowed to polymerize with tumbling in a −20° bath for twenty-four to forty-two and one-half hours. The latex formed was added with mechanical agitation to

Table II

Polymerization at −20°

Run	Polymerization time in hours	Conversion, %	Static solubility in benzene	[η]
1	42.5	69.2	81	5.08
2	42.5	69.2	80.5	5.05
3	24	36.5	92	4.12
4	24	36.5	92	4.07
5	31.5	58.5	90.5	4.87
6	31.5	58.5	91.5	4.90

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(1) This investigation was carried out under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the Government Synthetic Rubber Program.

(2) Hobson and D'Ianni, *Ind. Eng. Chem.*, in press.