SHORT COMMUNICATIONS

ACRYLONITRILE POLYMERISATION WITH VARIOUS REDUCING ACTIVATORS

FAZAL HUSSAIN, A.J. AHMED and K. NABI

Institute of Chemistry, University of Panjab, Lahore

(Received February 6, 1968)

During the past thirty years, the polymerisation of acrylonitrile has attracted much attention.[1–5]

The present work records the effect of reducing agents on the polymerisation of acrylonitrile initiated by potassium persulphate in aqueous solution at 32°C. The effect of pH was seen in particular. The idea was to find out appropriate reducing activators which should be more economical and should give maximum yield. The effect of nitrates of Ca, Ba, Sr, Cd and Mg on the polymerisation has also been studied both in acidic and alkaline media. The outstanding feature of the technique from a practical point of view is that it enables polymerisation to be performed at much greater speed than can be achieved by conventional methods and the polymer produced being of high molecular weight finds applications in rubber, plastic and fibre-forming materials.

Experimental

Materials.—Acrylonitrile (B.D.H.) was purified in the manner as mentioned earlier.[6] Potassium persulphate and the reducing agents given in Table 1 were of AnalaR grade and were used without further purification. Water used throughout this work was of conductivity grade and was obtained by passing laboratory distilled water through a 5-ft column packed with Biodeminpolit ion exchange resin. Nitrogen supplied by Pakistan Oxygen Company was purified as described in earlier work.[7]

Procedure.—The apparatus used for studying the aqueous polymerisation resembled that of Bacon[1] but in a modified form. The desired amounts of water, acrylonitrile and reducing activator (1 mole per mole of $K_2S_2O_8$) were taken and the pH of the mixture was noted by the Cambridge pH indicator. The mixture was then charged in a gas-tight 500-ml Pyrex flask placed in the thermostat at 32±0.1°C. It was stirred by an electrical stirrer and a brisk stream of purified nitrogen gas was allowed to pass through the mixture for 10–15 min to displace air or oxygen which acts as an inhibitor and then its rate was reduced to about one bubble per sec. The required amount of $K_2S_2O_8$ in concentrated aqueous solution form was then added into the reaction flask.

The induction period was measured by the interval between adding $K_2S_2O_8$ solution and first observing turbidity in the solution. Polymerisation time was measured from the end of the induction period. At any time interval a sample could be expelled out if desired under gentle nitrogen pressure by suitably adjusting the taps, into a weighed beaker for pH measurement.

After the required period of polymerisation the reaction was stopped and the flask contents were filtered through a weighed sintered crucible. After washing the polymer repeatedly with distilled water and methyl alcohol, it was dried at 110°C to a constant weight and the % polymerisation was calculated.

TABLE 1.—EFFECT OF ACTIVATING AGENTS ON THE PERSULPHATE-CATALYSED POLYMERISATION OF ACRYLONITRILE IN AQUEOUS SOLUTION.*

No.	Activating agent	Activating agent mole used per mole $K_2S_2O_8$	pH after mixing all components except $K_2S_2O_8$	pH after 1 hr polymerisation	Induction period	Monomer polymerised (%)
(1)	(2)	(3)	(4)	(5)	(6)	(7)
1	None	—	4.2	3.9	31 min	1.53
	,,	—	6.0	5.4	30 ,,	1.61
2	$TiCl_2$ (B.D.H)	1.0	2.9	2.7	2 ,,	slight turbidity

(*Table Continued*)

(*Table Continued*)

(1)	(2)	(3)	(4)	(5)	(6)	(7)
	$TiCl_2$ (B.D.H.)	1.0	5.0	4.6	7 ,,	slight turbidity
3	$Na_2S_2O_5$ (B.D.H.)	1.0	3.5	3.2	0 ,,	85.7
	,,	1.0	6.2	6.0	0 ,,	85.8
	,,	1.0	8.7	8.9	1 ,,	56.4
	$K_2S_2O_5$ (B.D.H.)	1.0	3.5	3.1	0 ,,	76.9
	,,	1.0	6.2	5.9	0 ,,	79.6
	,,	1.0	8.7	8.9	1 ,,	32.8
4	H_2S (Lab.)	Brisk stream	3.4	3.1	0 ,,	0.1
	,,	,,	6.2	6.0	0 ,,	0.15
	,,	,,	10.2	10.4	0 ,,	slight turbidity
5	$Ca(NO_3)_2$ (E. Merck)	1.0	6.7	6.6	4 hr	None
	,,	1.0	4.0	3.8	4 ,,	,,
	,,	1.0	10.0	10.1	4 ,,	,,
	$Ba(NO_3)_2$ (E. Merck)	1.0	6.7	6.7	4 ,,	,,
	,,	1.0	4.0	3.9	4 ,,	,,
	,,	1.0	10.0	10.1	4 ,,	,,
	$Sr(NO_3)_2$ (E. Merck)	1.0	6.7	6.7	4 hr	None
	,,	1.0	4.0	3.9	4 ,,	,,
	,,	1.0	10.0	10.1	4 ,,	,,
	$Cd(NO_3)_2$ (E. Merck)	1.0	6.7	6.6	4 ,,	,,
	,,	1.0	4.0	3.9	4 ,,	,,
	,,	1.0	10.0	10.2	4 ,,	,,
	$Mg(NO_3)_2$ (E. Merck)	1.0	6.7	6.7	4 ,,	,,
	,,	1.0	4.0	3.9	4 ,,	,,
	,,	1.0	10.0	10.1	4 ,,	,,
6	$C_6H_{12}O_6$ (Pak made M.I. Chem Co)	1.0	4.0	3.7	1 min	6.8
	,,	1.0	6.0	5.8	1 ,,	7.9
	,,	1.0	9.0	9.3	1 min	1.2
7	$C_6H_4CH_3SO_2OH$ (B.D.H.)	1.0	2.0	1.8	50 ,,	1.0
	,,	1.0	7.0	6.1	36 ,,	3.6
	,,	1.0	10.0	10.3	2 hr	slight turbidity
8	KCNS (B.D.H.)	1.0	2.6	2.0	1/3 ,,	29.3
	,,	1.0	6.0	5.7	1 ,,	41.2
	,,	1.0	10.0	10.1	1½ ,,	6.2

*The polymerisation system consisted of: Water 200 g, Acrylonitrile 10.0 g, Potassium persulphate 0.4 g, +Activating agent (as shown above).

Polymerisation was conducted under nitrogen pressure, with slow stirring at 32±0.1°C for 1 hr from the end of the induction period.

Discussion

In the present work the system (M+IR) is used, where M is the monomer, I is an initiator and R is a reducing activator, that is any substance which is capable of catalysing the reaction. The pH was maintained with H_2SO_4 and NaOH and its effect was observed on the rate of polymerisation of the reaction mixture whose pH was measured before and after the polymerisation. It is found that the acidic condition is the prerequisite for such a system. Maximum yield was 86% with $Na_2S_2O_5$ at pH 6.2. Nitrates of the metals of second group were also employed as reducing activators at different pH and it was observed that the induction period remains the same from Ca to Cd with a little polymerisation. In the case of H_2S colloidal sulphur is liberated and perhaps this hinders the polymerisation rate as was concluded from the little polymerisation. TiCl2, $C_6H_4CH_3SO_2OH$, $C_6H_{12}O_6$, 2(COOH) H_2O were also employed at different pH values; results obtained with these are not encouraging. KCNS used gave 29.3 and 41.2% polymer at pH 2.6 and 6.0 respectively.

References

1. R.G.R. Bacon, Trans. Faraday Soc., **42,** 140 (1946).

2. L.B. Morgan, Trans. Faraday Soc., **42,** 169 (1946).
3. T. Alfrey, C.G. Overberger and S.H. Pinner, J. Am. Chem. Soc., **75,** 4221 (1953).
4. Thomas, Greason and Pellion, Proc. Roy. Soc., **A24,** 43 (1957).
5. F.S. Dainton, P.H. Seaman and D.G.I. James, J. Polymer Sci., **34,** 209(1959).
6. F. Hussain, M.F. Butt and S.U. Haider, Pakistan J. Sci. Ind. Res., **10,** 143 (1967).
7. F. Hussain, A. Rashid and M. Amjad, Pakistan J. Sci Ind. Res., **11,** 134 (1968).

ALKALOIDS OF CORYDALIS STEWARTII FEDDE: CORYDININE

G.A. MIANA, M. IKRAM and S.A. WARSI

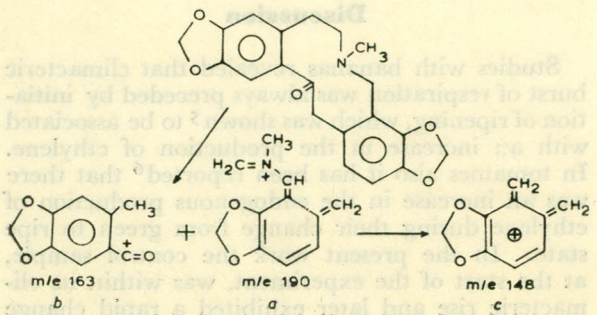
North Regional Laboratories, Pakistan Council of Scientific and Industrial Research, Peshawar

(Received July 15, 1968)

Three alkaloids, named and formulated as corycidine $(C_{11}H_{11}O_4N)_2$, m.p. 290–292°C (dec.), corydinine, $C_{17}H_{17}O_4N$, m.p. 199–200°C, and corydicine, $C_{19}H_{17}O_5N$, m.p. 181–182°C, were isolated from *Corydalis stewartii* Fedde.[1] All the three alkaloids were reported[1] to contain methylene-dioxy groupings and tertiary nitrogen atoms. Evidence is presented in this paper which identifies corydinine as protopine(I).

The IR spectrum of corydinine showed bands at 3040, 2945, 2890, 2850, 1657, 1620, 1610, 1500, 1450 and 1375 cm^{-1}. The presence of a very strong band at 1657 cm^{-1} suggested[2] it to belong to cryptopine type alkaloids. The UV spectrum in ethanol showed a maximum at 292 mμ ($\log\varepsilon$ 3.92) which indicated[3] that the alkaloid might be protopine (I).

The mass spectrum of corydinine showed prominent peaks at m/e 353 (M^+), 338 (M–15), 190 (*a*), 163 (*b*), 148 (*c*), 42 and 18. The molecular ion peak at m/e 353 suggested a molecular formula, $C_{20}H_{19}O_5N$ for corydinine. The mass spectral fragmentation pattern[4] alone, suggests protopine (I), m.p. 204–205°C[5] structure for corydinine.



The NMR spectrum in deuterated chloroform of corydinine is also in excellent agreement with the protopine structure. Thus, major peaks at 2.08 (3H, singlet, one N-methyl), 7.45 (2H, multiplet, one methylene), 7.12 (2H, multiplet, one methylene) 6.42 (2H, singlet, one methylene), 6.22 (2H, singlet, one methylene), 4.08–4.04 (4H, two close doublets, two methylenedioxy groupings), 3.35, 3.31 and 3.09τ (4H, aromatic protons) accounts for almost all the nineteen protons of protopine.

In view of the above, it is suggested that corydinine is identical with protopine.

The IR, UV, NMR and mass spectrum of corydicine is also similar to those of corydinine (or protopine) except for an additional band at 1755 cm^{-1} in IR and some unidentified peaks in NMR spectrum, which strongly suggests that corydicine may be a mixture of protopine and a phthalid-isoquinoline type alkaloid. Studies are in progress on its purification and characterisation.

Acknowledgement.—The authors are very grateful to Dr. P. Bravo, Istituto di Chimica, Politechnico di Milano, Milano, Italy, for IR, UV, NMR and mass spectra.

References

1. M. Ikram, M.E. Haque and S.A. Warsi, Pakistan J. Sci. Ind. Res., **9,** 34(1966).
2. D.A. Ramsay and R.N. Jones, J. Am. Chem. Soc., **73,** 305(1951).
3. A.W. Sangster and K.L. Stuart, Chem. Rev. **65,** 69(1965).
4. L. Dolejs, V. Hanus and J. Slavik, Coll. Czech. Chem. Commun., **29,** 2479 (1964).
5. T.A. Henry, *The Plant Alkaloids* (J.A., Churchill Ltd., London, 1949), fourth edition, p. 299.

EFFECT OF THE SUPPRESSED CLIMACTERIC RISE ON THE RIPENING CHANGES OF LYCOPERSICUM ESCULENTUM

M.H. QUAZI,* and H.T. FREEBAIRN

Department of Biology, University of Houston, Houston, Texas 77004, U.S.A.

(Received April 13, 1968)

Ripening of climacteric fruits have always been found to be associated with the climacteric burst of respiration.[1] Tomatoes exhibit a similar

*Now at Jamia Millia College, Malir, Karachi.

behaviour. Studies with banana, another climacteric fruit, revealed that once the fruit was initiated to ripen, its ripening changes were determined not by the climacteric burst of respiration but by its endogenous production of ethylene.[5] This departure of banana from the reported behaviour suggested that the ripening changes in tomatoes may also be determined by its endogenous production of ethylene rather than the climacteric burst of respiration. Preliminary work was therefore undertaken to suppress the climacteric rise by using low oxygen concentrations and to observe the effects of the suppressed climacteric rise on ethylene production and ripening behaviour of tomatoes.

Material and Method

Mature hard green tomatoes were obtained from the wholesale market. Since their exact age was not known the sampling was done on the basis of their relative size and colour.

The desired gas mixtures were prepared in the laboratory by introducing measured amounts of pure nitrogen, oxygen and ethylene in cylinders previously evacuated by a vacuum pump. The gas mixtures consisted of 2.5% oxygen with and without 100 p.p.m. ethylene. Final analysis of the gas in the cylinder was carried out by an Orsat analyser using a 100-ml burette. A similar cylinder filled with air was used as a control.

For initiating the ripening of fruit, the entire sample was first subjected to an air stream containing 100 p.p.m. of ethylene for a period of 24–36 hr. A weighed amount of initiated fruit, which was still hard and green, was then transferred to sealed dessicators. Each dessicator was seperately connected to a cylinder filled with the desired gas mixture. In order to ensure that no ethylene was left in the intercellular spaces of fruit, air from each dessicator, at the start of the experiment was removed with a vacuum pump twice. Leaks were tested with a mercury manometer. The gas mixture from the cylinder was then flushed at a constant rate of 0.3 ft^3/hr. Outflowing gas from the dessicator was sampled with a 25-ml syringe and introduced in a gas chromatograph, where the amount of carbon dioxide was detected with a thermal conductivity detector and an 8-inch 30–60 mesh sillica gel column. The rate of respiration was determined on the basis of ml of carbon dioxide produced/hr/kg weight of fruit. The ripening was determined by colour grade as reported by Pratt and Workman.[4] The experiments were conducted at a constant temperature of 68°F in a growth chamber.

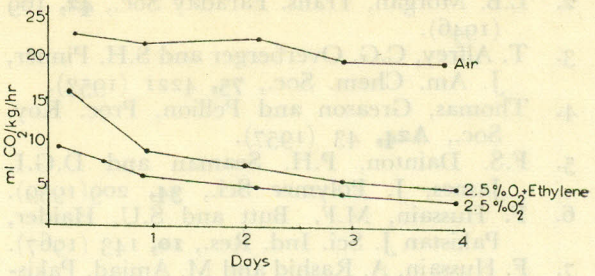


Fig. 1.— The rate of CO_2 evolution in the gas mixtures.

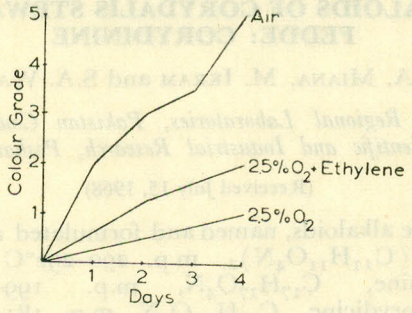


Fig. 2.— The rate of colour change of fruit in the gas mixtures.

Results

Analysis of Figs. 1 and 2 shows the following features:

1. The control sample at the start of the experiment was within its climacteric rise and exhibited a rapid rate of colour change.

2. Lowering of oxygen caused a steady decline in the rate of respiration and the climacteric rise was greatly reduced. The sample still exhibited definite signs of ripening as evidenced by its change of colour.

3. Presence of ethylene with low oxygen concentration did not alter the respiratory behaviour of the fruit. The climacteric rise was still reduced as in the previous sample. The fruit, however, exhibited an accelerated rate of colour change.

Discussion

Studies with bananas revealed that climacteric burst of respiration was always preceded by initiation of ripening, which was shown[5] to be associated with an increase in the production of ethylene. In tomatoes also it has been reported[6] that there was an increase in the endogenous production of ethylene during their change from green to ripe state. In the present work the control sample, at the start of the experiment, was within its climacteric rise and later exhibited a rapid change

of colour grade. This suggested that the fruit had been initiated to ripen and its endogenous production of ethylene had increased. The presence of 2.5% oxygen surrounding the sample suppressed the climacteric rise of respiration but did not stop its ripening. It may be proposed that lowering of oxygen concentration after initiation of ripening could not inhibit the endogenous production of ethylene, as was found in the earlier work with bananas. Consequently the ripening was observed even in the absence of a definite climacteric rise. Previous studies[5] also showed that lowering of oxygen concentration after initiation of ripening resulted in a corresponding decrease in the rate of ethylene evolution. The slow rate of colour grade in fruits under reduced oxygen level may therefore be attributed to the decreased production of ethylene. This assumption is further supported by the fact that exogenously supplied ethylene with low oxygen concentrations did not alter the respiratory behaviour of fruit but accelerated the rate of colour grade. It appears likely that ripening of tomato is associated with the endogenous production of ethylene rather than the climacteric burst of respiration.

The exact role of climacteric rise in the ripening of fruit is not clearly understood. A number of physiological changes, such as softening of flesh, destruction of chlorophyll, conversion of pectin from the insoluble state to soluble state, disappearance of starch, accumulation of sugars and an increase in the net protein content of fruit, have been reported to be associated with the climacteric rise of respiration.[1] The fact that normal ripening of tomato, as indicated by its colour, texture and flavour was observed with a reduced climacteric rise suggested that the ripening changes were not necessarily controlled by the climacteric burst of respiration. On the contrary, the observation that exogenously supplied ethylene accelerated the fruit colour, suggested that the ripening was associated with the endogenous production of ethylene whether the climacteric occurred or not.

References

1. J.B. Biale, Respiration of fruit in Handbuch Der Pflanzenphysiologie, **12,** 536 (1960).
2. F.G. Gustafson, Am. J. Bot., **23,** 441 (1936).
3. P.K. Heinz and C.C. Craft, Proc. Am. Soc. Hort. Sci., **62,** 397 (1953).
4. H.K. Pratt. and M. Workman, Proc. Am. Soc. Hort. Sci., **81,** 467 (1961).
5. M.H. Quazi, and H.T. Freebairn, *Masters's Thesis. University of Houston,* Houston, Texas (1967).
6. M. Workman, and H.K. Pratt, Plant Physiol. **32,** 330 (1957).

BOOK NOTICES

Heterocyclic Chemistry. Adrien Albert, 569 pp. The Athlone Press, University of London, 1968. Second edition.

Current estimates indicate that some 65% of all published work in organic chemistry, deals with some aspect of heterocycles. In spite of it, textbooks on this subject covering basic principles of structure, properties, and synthesis are not only of very recent origin but often fall below the standard set for textbooks in the general field of organic chemistry. This book adequately meets this need. Although intended primarily to be an introductory course on the subject, the text is also designed to help more advanced readers, among whom the special needs of research workers in biology and medicine have been kept in view. The book is mainly concerned with the substances having nitrogen, oxygen, or sulphur as the hetero-atom. It is not a collection of topics on individual heterocycles but in this book an overall view of the subject has been taken. The readers' understanding of the main characteristics of paraffinic, ethylenic and aromatic compounds is used as a basis for subdividing heterocyclic chemistry into the same three divisions. The heteroaromatics have further been divided into (i) π-deficient heterocycles (e.g. pyridine), i.e. substances allied to nitrobenzene in their electronic structure, and (ii), π-excessive heterocycles (e.g. pyrrole, furan, thiophen), i.e. substances allied to aniline. The book has two parts. The nine chapters of the first part deal with (i) The scope of the subject, and of the book, (ii) Paraffinic Heterocycles, (iii) Introduction to Heteroaromatics, (iv) π-Dificient *N*-Heteroaromatics, (v) π-Excessive *N*-Heteroaromatics, (vi) π-Excessive *O*-and *S*-Heteroaromatics, (vii) Introduction to Ethylenic Heterocycles, (viii) Ethylenic Heterocycles (I)—Partly Hydrogenated Heteroaromatic and (ix) Ethylenic Heterocycles (II)—Pyrans and related substances; Six-membered rings containing oxygen or sulphur. In these chapters after a brief introduction, the major part is devoted to the subject of correlation