Mechanism of Charge-transfer Polymerization: 3,5,6-Trichloro-2-hydroxy-1,4-benzoquinone as an Acidic Impurity in *p*-Chloranil

By TADAO NATSUUME, YASUHIKO SHIROTA,* HIROTAKA HIRATA, SHIGEKAZU KUSABAYASHI, and HIROSHI MIKAWA
(*Department of Chemical Technology, Faculty of Engineering, Osaka University, Yamada-Kami, Suita, Osaka* 564, *Japan*)

WE reported[1] that trace acidic impurities are tenaciously retained in *p*-chloranil purified by ordinary methods and are mainly responsible for the "charge-transfer" polymerization of *N*-vinylcarbazole by *p*-chloranil.

We have isolated and identified the main component of the acidic impurities. Commercial "pure" grade *p*-chloranil[2] was chromatographed (benzene–calcium carbonate) and the pink-violet top zone was eluted with water. The aqueous solution was evaporated and extracted with benzene A yellow-orange compound was isolated, purified by vacuum sublimation, m.p. 199° (decomp.), and identified as 3,5,6-trichloro-2-hydroxy-1,4-benzoquinone (X) (i.r., u.v., mass spectra, and mixed m.p.[3]). The commercial "guaranteed reagent" *p*-chloranil contained (spectroscopically) *ca.* 0·25% of (X). Trichlorohydroxyquinone (X) was likewise detected from *p*-chloranil purified by recrystallization or sublimation. Water-extraction of a benzene solution of commercial "pure grade" *p*-chloranil also gave acidic impurities, among which (X) was the main component. *p*-Chloranil itself is unaffected by all the procedures described above.

Trichlorohydroxyquinone (X) initiates the cationic polymerization of *N*-vinylcarbazole as shown in the Figure (curves 3, 4, and 5), thus indicating that the "charge-transfer ' polymerization of *N*-vinylcarbazole by *p*-chloranil is mainly cationic and initiated by the impurity.

(*Received, January 20th,* 1969; *Com.* 085.)

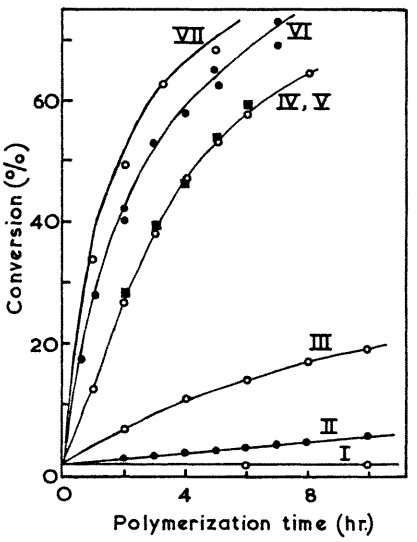

FIGURE. *Polymerization of* N-*vinylcarbazole by* p-*chloranil* (C) *and* 3,5,6-*trichloro*-2-*hydroxy*-1,4-*benzoquinone* (X). (*Monomer concentration,* 0·5M. *Catalyst concentration* [ ]M) (I), *benzene,* 25°, [C][a] 2×10^{-2}; (II), *benzene,* 80°, [C][a] 2×10^{-2}; (III), *benzene,* 80°, [X] 4×10^{-6}; (IV), O, *benzene,* 80°, [X] 5×10^{-5}; (V), *benzene,* 80°, [C][a] 2×10^{-2} admixed with (X), [X] 5×10^{-5}; (VI),[1] *benzene,* 80°, [C][b] 2×10^{-2}; (VII)[4], *toluene,* 80°, [C] $1{\cdot}2 \times 10^{-2}$.

[a] *p*-Chlonanil was once recrystallized from benzene and then passed through a column of calcium carbonate, followed by two recrystallizations from benzene and one sublimation *in vacuo*.

[b] *p*-Chloranil, "guaranteed" reagent, was recrystallized once from benzene.

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