

## JOHN WILLIAM BAKER AND THE ORIGIN OF THE BAKER-NATHAN EFFECT

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The Baker-Nathan effect was a theory proposed by John William Baker (1898-1967) and Wilfred Samuel Nathan (1910-1961) of Leeds University in 1935 to explain certain anomalous results obtained in  $\text{SN}_2$  reactions carried out in solution. The explanation produced by them was expanded to a general type of no-bond resonance known as hyperconjugation by Mulliken in papers published in 1939 and 1941 (1). Hyperconjugation is today defined as the conjugation of polarized sigma bonds and adjacent pi orbitals. This theory has been applied to a host of anomalous physical measurements such as bond lengths and dipole moments. The Baker-Nathan effect as it was originally framed is no longer used in light of more plausible explanations for rate accelerations in solution.

This paper will first deal with the life of John William Baker, a name that is far from familiar to most chemists today. Those chemists who received their training in physical organic chemistry in the pre-1975 era probably remember the Baker-Nathan effect. The paper will then examine how Baker and his collaborator Nathan discovered what was believed to be the first example of hyperconjugation. Next it will briefly discuss the downfall of the Baker-Nathan effect as an explanation of what happens in unexpected rate accelerations in reactions in solutions. A brief discussion of the concept of hyperconjugation as used today will conclude this paper.

### John William Baker

John William Baker was born in London on March 10, 1898, and he attended the Latymer Upper School, an

independent school in west London from 1909-1916. He was awarded a Royal Scholarship in Chemistry which allowed him to enroll at the Imperial College of Science and Technology in London. His exceptional aptitude for chemistry was shown by his passing the intermediate exams for the B.Sc. Degree by the end of 1916. In April 1917 he was conscripted and assigned to the Royal Engineers where he was commissioned a Lieutenant. His major responsibilities were in the area of water purification. In May 1918 he was sent to Mesopotamia (now Iraq) where he was assigned the same duties. He was finally demobilized in 1920 and returned to Imperial where he was awarded his B.Sc. with first class honors in 1921. The M.Sc. was awarded in 1923, a Ph.D. in 1925 and D.Sc. in 1928. His dissertation was nominally supervised by Jocelyn W. Thorpe (1872-1940) (2) but most directly by Christopher K. Ingold (1893-1970) (3).

Jocelyn Thorpe worked in the laboratory of Victor Meyer in Heidelberg under the guidance of Karl von Auwers. He was awarded his D.Phil. in 1895 and then assumed a junior position at Owens College in Manchester under W. H. Perkin Jr. (1860-1929). In Manchester in addition to his teaching duties he worked on a variety of synthetic organic problems. He stayed until 1909 when he was awarded the Sorby Research Fellowship at the University of Sheffield. Freed from any teaching or administrative duties, he was able to produce a large body of research which led in 1913 to his being offered the professorship in organic chemistry at Imperial College.

In Thorpe's first year at Imperial, Ingold, after completing undergraduate studies in Southampton joined his

research group and quickly established himself as both a first class researcher and an innovative thinker. As part of the war effort Ingold was involved in the production of tear gas and other related work at the Cassel Cyanide company in Glasgow. When the war ended there seemed little possibility of Ingold entering the realm of academia and so he stayed at Cassel for another two years. In 1920 Thorpe was able to secure Ingold a position as a lecturer in organic chemistry at Imperial. In the postwar years there were two major research programs that Thorpe carried on with the assistance of Ingold: the effect of alkyl substitution on ring closure, which led to the Thorpe-Ingold principle, and ring-chain tautomerism.

Baker was supervised by Ingold and the two papers he jointly published with Thorpe and Ingold reflect this program. The first was in 1923 and dealt with ring closure, and the second in 1924 was concerned with ring-chain tautomerism (4). In 1925 the possibility of a university position of any sort for Baker was bleak to say the least. As a matter of necessity he accepted the position of Senior Chemistry Master at the North-Eastern County School in Barnard Castle in the northeast of England. However his days as a schoolmaster were very brief due to the meteoric rise of Ingold in British chemistry. At the unheard-of age of 30, Ingold was elected a Fellow of the Royal Society and was offered the professorship at Leeds University vacated by the retirement of J. B. Cohen (1859-1935).

Ingold was allowed to pick his own staff and he assembled a first class group of investigators as junior members. Baker was hired as an assistant lecturer, and the group grew to have several future notables in British chemistry such as Harold Burton (1901-1966) and Charles W. Shoppee (1904-1994). During Ingold's brief six-year tenure at Leeds which lasted until 1930 when he left for University College London, there were three ongoing areas of research. The first was aromatic substitution and the mechanism of aromatic side-chain reactions. The second dealt with anionotropic change, which was part of his continuing interest in the ionic mechanism of tautomerism. The third research program dealt with the effects of polar substituents on the velocity and orientation in addition reactions to unsaturated systems.

Baker published six papers during the Ingold time at Leeds. Three of these dealt with the nature of the alternating effect; one involved ring-chain tautomerism; and two involved ring formation (5). These were sufficient for him to be awarded the D.Sc. degree by University of London in 1928. Baker was never involved in the ongoing

acrimonious debate that occurred between Ingold and Robinson concerning the application of the electronic theory to aromatic substitution in the late 1920s.

In 1930 Robert Robinson resigned his professorship at University College London to become the Waynflete Professor of Organic Chemistry at Oxford. Ingold was offered the position Robinson vacated, and he immediately accepted the chance to return to London from Leeds, which in the 1920s was a very grimy industrial city with very unhealthy air quality. The conditions of Ingold's employment at University College would not let him bring any of his team with him. The only person who did go to London was Christopher L. Wilson who was finishing his B.Sc. and wished to do his Ph.D. under Ingold at University College. Ingold was strongly in favor of Baker becoming his successor at Leeds (6) but the professorship went instead to Frederick S. Challenger (1887-1983), a natural products chemist from the University of Manchester. Challenger had joined the staff in Manchester in 1920 and had worked with Robinson. Baker, Shoppee, and Burton among others were in Shoppee's words "left high and dry in the provinces" (7). Challenger had no problem with Baker continuing his line of research in physical organic chemistry. Baker would remain at Leeds for the balance of his academic career, ultimately becoming the Reader in the Mechanism of Organic Reactions. He did apply for several professorships during his time at Leeds. In 1943 he was considered for the professorship at University College, Bangor, but the appointment was given to Edward D. Hughes instead. Baker was never elected a Fellow of the Royal Society either, which was surprising given his research output and the difficult circumstances in which this research was conducted, namely economic depression, war, and post-war austerity.

In his career Baker published over 100 papers of which 76 appeared in the *Journal of the Chemical Society*. In 25 of his *J. Chem. Soc.* papers he was the sole author. In addition he was the author of four monographs and books. These were *Natural Terpenes* (1930) (8), *Tautomerism* (1934) (9), *Hyperconjugation* (1953) (10), and *Electronic Theories of Organic Chemistry* (1958) (11). His *Hyperconjugation* has the following dedication in the preface: "To Christopher Kelk Ingold in grateful appreciation of his inspiring friendship throughout my career."

When Ingold left Leeds in 1930 Baker took over his teaching duties in the first-year organic chemistry course. His approach followed that of Ingold and in essence he was Ingold's man in the northeast of England



Figure 1. Group photo from Baker's time at Leeds

for the physical organic approach to organic chemistry rather than repetition of endless facts with no obvious connection which was so typical of the time. However Baker's reverence for Ingold caused him to ignore other important changes that were going on, and his course did not substantially change in content for over 27 years. What was revolutionary in 1930 was dated by 1957 when the newly appointed professor of organic chemistry Basil Lythgoe removed Baker from the course. This was not taken very well by Baker, who resigned in 1959 ostensibly because of the ill health of his wife. When his wife died in 1962 he moved to York where his only child, a son, lived. He remarried and became very active in the Congregational church, devoting his final years to church work. He died on May 12, 1967.

Wilfred Samuel Nathan was born in December 1910 in Cardiff, the son of parents who immigrated to Wales from the continent. He obtained his Ph.D. at University College, Bangor, under the supervision of the noted physical organic chemist Herbert Ben Watson in 1935. With support from a Department of Scientific and Industrial Research grant he was able to work with Baker in Leeds for one year. When this grant expired Nathan moved to Ingold's group at University College London where he was supported by a grant from Imperial Chemical Industries. In 1936 he accepted a position with British Petroleum (BP) at their laboratory in Llandarcy, Wales. He was transferred in 1941 to BP's facility at Sunbury-on-Thames near London and spent the rest of his professional career there. At BP he worked in a variety of areas including thermal diffusion, the behavior of waxy crude oils and

the mechanism of wear in engines. He died on August 6, 1961, from complications following surgery.

### How the Baker-Nathan Effect Was Discovered

In a paper published in 1935 in the *Journal of the Chemical Society* bearing the title "The Mechanism of Aromatic Side-chain Reactions with Special Reference to the Polar Effects of Substituents. Part V. The Polar Effects of Alkyl Groups," (12) we find the first discussion of what came to be known as the Baker-Nathan effect. This paper was a study of the Menshutkin reaction between *p*-substituted benzyl bromides and pyridine in dry acetone. This is an example of a class of  $S_N2$  reaction where the reactants are both neutral. The results did not conform to the usual order of reactivity expected. Ingold had discussed the effect of alkyl substituents on  $S_N2$  reactions in terms of the positive inductive effect (+I) at a saturated carbon atom. Thus one would expect that the order of alkyl groups based on electron releasing abilities would be  $t\text{-Bu} > i\text{-Pr} > \text{Et} > \text{Me} > \text{H}$ .

This had been experimentally proven to be the case in several studies done prior to 1935. The experiments undertaken by Baker and Nathan introduced a new scenario in that the alkyl group was part of a conjugated system. To rationalize their results Baker and Nathan contemplated the possibility that a resonance effect or mesomeric effect to use Ingold's terminology was also operating in this case in addition to the inductive effect.

Ingold in his 1934 *Chemical Reviews* paper "Principles of an Electronic Theory of Organic Reactions"

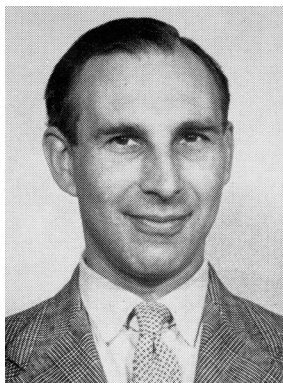
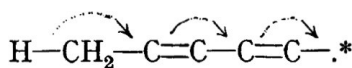


Figure 2. Nathan's photo from his obituary from the BP Shield

(13) discussed the various types of electronic effects that could occur to explain the mechanisms of organic reactions. Baker and Nathan used the Ingold nomenclature as the basis to explain the anomalous behavior of the methyl group (12):

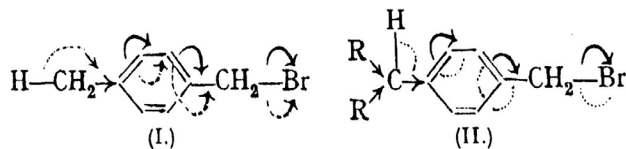
It is tentatively suggested that, *when the methyl group is attached to a conjugated system* [italics in original], the duplet of electrons forming the C–H bond in this group are appreciably less “localized” than are those in a similarly placed C–C bond. This means that a methyl group, attached to the necessary system, is capable of permitting electron-release by a mechanism which, in essentials, is a type of tautomeric effect,



The asterisk refers to a note at the bottom of the page which reads as follows: “The original suggestion that such a polar effect is present was due to W. S. N.”

How Nathan came up with the idea we do not know but considering that Nathan was a relatively young man and had been a student in the early 1930s when both valence bond theory and molecular orbital theory had been developing, he may have been influenced by these new ideas. The caveat was made that this new effect was in addition to the normal positive inductive effect (+I) of alkyl groups.

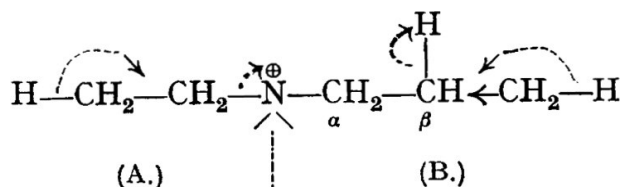
The rationale that was presented by Baker was that if methyl increased the rate of  $\text{SN}_2$  reaction in benzyl systems and *tert*-butyl had the least effect this must be due to the lack of what came to be known as hyperconjugation. When a conjugated system is not present, then the normal inductive effect occurs and the rates are reversed. This argument can be clearly seen in the following diagram included in the text. The ordinary inductive effect is in-



dicated by fully pointed arrows and the hyperconjugative effect by the dotted arrows.

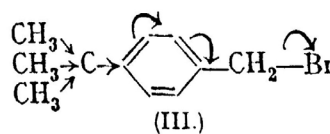
This new effect was used by Baker and Nathan in the same paper to explain the Hofmann degradation reaction of quaternary ammonium hydroxides. When ethyl dimethyl propylammonium hydroxide is subjected to the Hofmann degradation reaction it produces ethylene as predicted. Baker and Nathan offered an explanation which invoked their newly discovered effect. The key to the path of the reaction is which of the hydrogen atoms

is removed by the hydroxide ion. As the C–H bond is being broken and negative charge is being built up, as in the case of the propyl group, the inductive effect of the methyl will intensify the negative charge and retard this hydrogen being lost. The ethyl group operates in such a way as to minimize the inductive effect and hyperconjugation will facilitate the breakage of the C–N bond to the ethyl group and the formation of the double bond in ethylene. These effects are illustrated in the following diagram from Baker and Nathan’s paper (12).



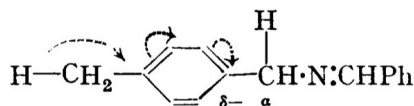
A further question that needed to be answered was whether the effect was, using the Ingold terminology, strictly a mesomeric effect (a permanent polarization effect also known as the resonance effect) or one that is an electromeric effect (a polarizability effect caused by an attacking reagent). In order to answer these questions Baker, Nathan, and Shoppee conducted a study “The Effects of *p*-Alkyl Substituents on Prototropy in the Methyleneazomethine System” (14). Prototropy is a special case of the general phenomenon of tautomerism, a subject that Baker was very familiar with from his previous work with Ingold and Thorpe.

Shoppee had shown in 1931 (15) that this reaction was favored by electron-withdrawing substituents (negative inductive effect, –I). These new studies of tautomerism in the azomethine system involved alkyl substituents only in the para position. Any alkyl group would be expected because of its +I (positive inductive



effect) to slow the rate of reaction as compared to the parent system. If the methyl group interaction involved a mesomeric (reso-

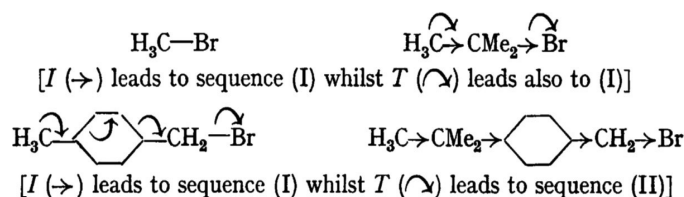
nance) effect (as in the diagram from Ref. 14) then it would be expected to retard the reaction to a greater extent than the *tert*-butyl group. This indeed is what was observed in the experiments performed.



There was still a lack of a clear-cut experimental

result which could show in a definitive manner that hyperconjugation was a real effect and not the result of some already known factor. Hughes, Ingold, and Taher tackled this question in a paper "Mechanism of Substitution at a Saturated Carbon Atom. Polar Effects in Alkyl Groups, as Illustrated by Solvolytic Substitutions of *p*-Alkylbenzhydryl Chlorides," published in 1940 in the *Journal of the Chemical Society* (16).

These investigators point out that in the displacement reactions in a series of simple alkyl bromides, the Baker-Nathan effect would operate in the same manner as the inductive effect. Thus it would be impossible to see if the effect is a real one. However, in the reactions of a *p*-alkyl benzyl bromide series, although the inductive effect and the tautomeric effect (Baker-Nathan) would reinforce one another, the order of reactivity would be different depending on which effect predominated. Not knowing whether the inductive effect or the tautomeric effect would be the most important, one would have difficulty in predicting the order of reactivity. If the Baker-Nathan effect is not real or is real but very weak, then the predicted order of reactivity would be  $\text{Me} < \text{Et} < i\text{-Pr} < t\text{-Bu}$  (sequence I in the following figure taken from Ref. 16), but if the Baker-Nathan effect is real and dominant, the order would be  $\text{H} < \{\text{Me} > \text{Et} > i\text{-Pr} > t\text{-Bu}\}$ .



The original report of the Baker-Nathan effect (12) was based on the study of an  $\text{SN}_2$  reaction in a series of compounds that did not give rise to large variations in the rates of reactions. For example, the difference between H and Me where one would expect both an inductive and tautomeric (hyperconjugative) effect was only 1: 1.65. As Ingold and his co-workers put it, "It is impossible to be confident that so closely spaced a rate series means what it may appear to mean" (16).

They explain the rationale for the study they are about to describe as follows (16):

What we need in order to get over the difficulty revealed in all this work is a device for making *one* of the four contributing factors (and it must be one of the two which involves alkyl conjugation) much greater than all others; and this can be done. We decide [*sic*] to study reaction rate in a *strongly*

electron-demanding reaction, and there can hardly be any reaction more suitable than a *unimolecular* nucleophilic substitution, where there is only a single electron-transfer involving carbon in the rate-affecting stage. [*italics in original*]

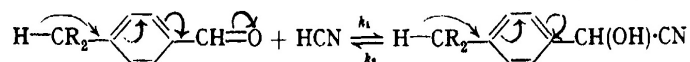
The reaction that was chosen for study was the hydrolysis of *p*-alkylbenzhydryl chlorides in 80% aqueous acetone, a reaction known to be of the  $\text{SN}_1$  type. If the Baker-Nathan effect was real then there would be a competition between the inductive effect and the conjugative Baker-Nathan effect. The key would be in the transition state where the conjugative effect would be paramount in lowering the energy of activation by electron transfer.

The results obtained by Hughes, Ingold and Taher (Table 1) were consistent with the order that would be predicted if the Baker-Nathan effect existed. This order was  $\text{H} < \text{Me} > \text{Et} > i\text{-Pr} > t\text{-Bu}$ . In addition to the large rate increase for Me vs H, all the other alkyl groups showed decreases with respect to Me in a regular manner as would be predicted by reduced hyperconjugative ability. "We regard this as the first satisfactory *evidence* of the reality of alkyl conjugation as envisioned by Baker and Nathan" (16).

**Table 1.** First-order Rate Constants and Arrhenius Parameters for the Hydrolysis of Benzhydryl Chloride and its *p*-Alkyl Derivatives (Table I of Ref. 16)

<i>p</i> -Substituent	H	Me	Et	<i>i</i> -Pr	<i>t</i> -Bu
$10^6 k \text{ (s}^{-1}\text{) at } 0.0^\circ\text{C}$	2.82	83.5	62.6	46.95	35.9
$10^{-11} A \text{ (s}^{-1}\text{)}$	1.91	1.23	2.19	3.47	4.07
$E \text{ (kcal mol}^{-1}\text{)}$	21.0	18.9	19.4	19.8	20.05

One further paper published by Baker in 1942 (17) should be mentioned. This dealt with the reaction of aldehydes to produce cyanohydrins as evidence for the mesomeric (hyperconjugative) effects of alkyl groups. Baker performed these studies to add further experimental evidence for the rate enhancement by methyl in contrast to *tert*-butyl when something other than the inductive effect is at work. Lapworth (18) had previously shown that in the equilibrium between *p*-substituted



benzaldehydes and their cyanohydrins that electron-releasing groups stabilized the aldehyde and destabilized the cyanohydrins. Baker studied the series of *p*-alkyl benzaldehydes where hyperconjugation was possible in the aldehydes but not in the cyanohydrins. He found that

the order of stability of the cyanohydrins with respect to their corresponding aldehyde was in the order  $H > t\text{-Bu} > i\text{-Pr} > Et > Me$ . It thus seemed that hyperconjugation was a real phenomenon.

Chemists increasingly used the Baker-Nathan effect to provide explanations for unusual patterns of rate enhancements and equilibrium as well as physical measurements such as bond lengths, dipole moments, and heats of hydrogenation to name a few. Two reviews of hyperconjugation were published in 1945 in *Chemical Reviews* (19) and in 1949 in *Quarterly Reviews of the Chemical Society* in 1949 (20), which gave an overview of how this effect was used to explain certain anomalies.

Table 2 lists references made to the Baker-Nathan effect and hyperconjugation in some popular texts of a more advanced nature published from 1943 to 1974. This is by no means a comprehensive listing, but it does provide evidence that the concept of hyperconjugation was taken seriously as a means of explanation in the chemical community.

In addition popular undergraduate textbooks such as Morrison & Boyd and Streitwieser & Heathcock of this period also mentioned the role of hyperconjugation as an explanation for certain anomalous experimental findings (22).

### What Happened to the Baker-Nathan Effect?

Today the Baker-Nathan effect is an historical footnote remembered by those who received their training in physical organic chemistry prior to the mid-1970s. During the mid-1950s there was great enthusiasm for using the Baker-Nathan effect as a way of explaining unexpected results when inductive effects were thought to be the driving force behind reactivity. One of the first to challenge this explanation was a paper published by Schubert and Sweeney in 1956. This paper with the in-

nocent enough title of "Concerning the Baker-Nathan Effect" offered an explanation based upon solvent effects (23). In this investigation of *p*-alkylbenzhydryl chlorides in 80% aqueous acetone it was shown that if the same reaction is carried out in the gas phase the order of reactivity was reversed with methyl now showing the least reactivity. Since the structure of the reactants was exactly the same the difference must be due to solvation effects and not to hyperconjugation in this case (23):

It should be made clear that the position being taken is not that C–H hyperconjugation is necessarily of no consequence, although the concept is not needed to explain the data cited here. The viewpoint is simply this: if the role of the solvent as discussed is of importance then other modes of electron release by alkyl

groups in the order *tert*-Bu > Me may be relatively more important, even when attached to an electron-demanding system.

This paper did not mark the beginning of a decline in the appearance of the Baker-Nathan effect in the chemical literature. Indeed, Schubert and Sweeney appear to have inspired a number of studies of solvent effects in connection with the Baker-Nathan effect. A search of SciFinder for the topic "Baker-

Nathan" shows more papers from the 1960s than any other decade and that about 1/3 of papers dealing with "Baker-Nathan" were papers published after 1956 and also concerned with solvents (24). Invocation of the Baker-Nathan effect in the chemical literature has dropped to practically nothing over the last 30 years, and some of those few papers that continue to treat it also continue to investigate the extent to which it can be attributed to solvent effects. For example, Conney and Happer looked at chemical shifts in  $^{13}\text{C}$  NMR in alkyl-substituted styrenes. They found that the order of substituent effect did not change in a variety of solvents ranging from non-polar to polar aprotic to polar protic, a result they interpreted as hyperconjugative because the solvent seemed not to matter much (25). Ten years later,

**Table 2.** Hyperconjugation references in some texts from 1943-1974 (21).

Text author and title	Year of publication	Number of pages devoted to hyperconjugation
Remick, <i>Electronic Interpretation of Organic Chemistry</i>	1943	10
Alexander, <i>Ionic Organic Reactions</i>	1950	8
Waters, <i>Physical Aspects of Organic Chemistry</i> (4th ed.)	1950	8
Gould, <i>Mechanism and Structure in Organic Chemistry</i>	1959	11
Fieser & Fieser, <i>Advanced Organic Chemistry</i>	1961	4
Hirsch, <i>Concepts in Theoretical Organic Chemistry</i>	1974	8

a computational chemistry paper by Exner and Böhm reported hyperconjugative stabilization in *p*-alkylbenzyl cations but not in the neutral parent hydrocarbons, concluding that the Baker-Nathan effect in solution kinetics must be a solvent effect (26).

in Figure 3 are “Ngrams,” plots of the frequency of occurrence of a word or phrase in the corpus of scanned books and journals at the Google Books project (27). The plots show that even at the height of their popularity, Baker-Nathan occurred in print more than an order of magnitude less frequently than did hyperconjugation.

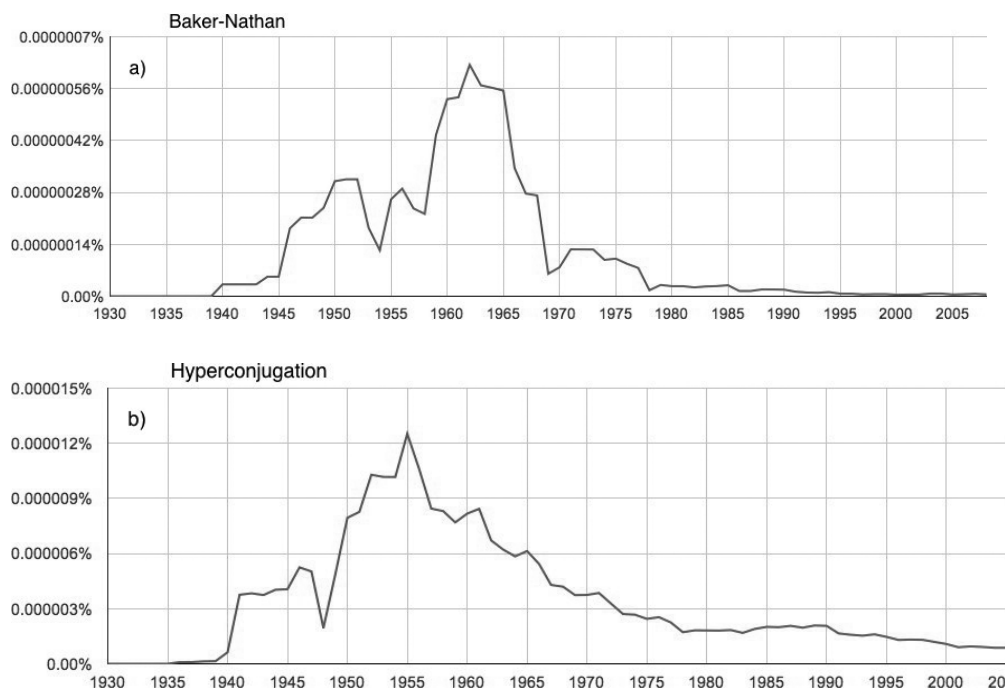


Figure 3. Ngrams for the terms (a) Baker-Nathan and (b) hyperconjugation (27).

The decline of the Baker-Nathan effect, then, does not appear to be a simple matter of displacement by a better explanation. In addition to questions about the source of the effect, other factors appear to include a restricted range of the term's usage as well as larger currents in physical-organic chemistry.

Some researchers have made a distinction between the Baker-Nathan effect and hyperconjugation, treating the latter term as a more general or theoretical concept and the former as a term of more restricted application. Exner and Böhm, for example, consider the Baker-Nathan effect as an empirical term restricted mainly to trends in reactivity (26). A related usage point can be seen in the title of Conney and Happer's paper, which refers to Baker-Nathan *order*, that is, to an empirical result (25).

Regardless of just how individual researchers have used the terms Baker-Nathan and hyperconjugation, the former was never as widely used as the latter. The graphs

Both terms have declined in frequency, which seems to suggest a move away from their subject matter in physical organic chemistry. Whereas Baker-Nathan has all but disappeared, hyperconjugation continues to appear in print.

It is difficult to be definitive, but it would seem that the disappearance of the Baker-Nathan effect from chemical literature is due to a combination of doubt over the utility of the concept in its original and rather restricted realm of application (reactivity in solution) and a shift in research interests in physical organic chemistry more widely. The concept of hyperconjugation is still used in certain contexts, and it remains a useful concept in education (28), even though the original Baker-Nathan effect has long passed into history of physical organic chemistry as a footnote. Although there is still controversy among theoreticians about hyperconjugation, Baker and Nathan as a result of their 1935 experiments opened a new way to explain many puzzling problems in organic chemistry.

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